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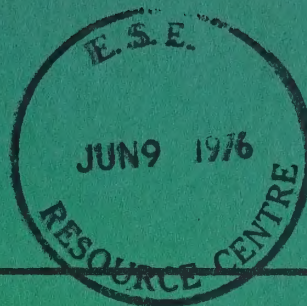
EPS 3-WP-76-5

REVIEW OF COLOUR REMOVAL TECHNOLOGY IN THE PULP AND
PAPER INDUSTRY, 1976.

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Review of Colour Removal Technology in the Pulp and Paper Industry

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Report EPS 3-WP-76-5

Water Pollution Control Directorate
April, 1976

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REVIEW OF COLOUR REMOVAL TECHNOLOGY
IN THE PULP AND PAPER INDUSTRY

by

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ABSTRACT

The pulp and paper industry produces large volumes of effluent containing, among other things, dark brown lignin and lignin degradation products. The exact nature of the chromophoric (colour causing) groups in the wastes and the effects of these colour bodies on the aquatic environment are not known. However, developmental work on several processes for colour reduction has reached full scale application and colour removal is now required in many local areas for various reasons.

Colour reduction can be achieved by either technical changes within the mill or by effluent treatment systems. In-plant modification can range from simple, inexpensive measures such as pulp washing and better "housekeeping" practices, to complex technological changes such as implementation of oxygen bleaching.

While in-plant changes should be considered and implemented as a first preference, external treatment may often still be required. There are a large number of external treatment methods which are known to be technically feasible for colour removal from pulp and paper mill effluents. Chemical treatment methods based on precipitation with Ca^{2+} , Mg^{2+} , Al^{3+} and Fe^{3+} have advanced to the stage of full scale application, as has the resin separation method of Uddeholm-Kamyr. The Rohm and Haas resin process, membrane processes (both ultrafiltration and reverse osmosis) and activated carbon adsorption have been tested on a large scale, while certain foam separation techniques, ozonation and extraction with amines have been examined on a smaller laboratory scale. These methods are known to be technically feasible, but the question of economics remains to be answered by further large and full scale testing. Several other methods have been and are being investigated. These include irradiation treatment, adsorption on fly ash and other waste materials, adsorption on activated alumina, land disposal, electrolysis and biological treatment.

Colour removal technology, although advancing rapidly, is still in its infancy. Many methods are known to work, but due to the wide range of effluents in the industry, no one method is likely to be applicable to all types. Therefore, research should continue to develop many viable alternatives for treatment. There is room for innovation in this aspect of wastewater treatment.

RÉSUMÉ

L'industrie des pâtes et papiers produit des effluents volumineux où l'on retrouve, entre autres, de la lignine brun foncé et de ses sous-produits. On ignore la nature exacte des groupes chromophores (agents colorants) présents dans ces déchets et leur effet sur le milieu aquatique. La mise au point de quelques procédés de décoloration a atteint le stade de l'application industrielle et, dans plusieurs localités, on exige maintenant et pour diverses raisons, la décoloration des effluents.

La décoloration peut s'obtenir par modification des procédés à l'intérieur des fabriques ou par traitement des effluents. Dans le premier cas, il peut s'agir de recours aussi simples et peu coûteux que le lavage des pâtes et un meilleur entretien, ou aussi complexe que la mise en oeuvre de blanchiment à l'oxygène.

Même si cela la solution préférable, il est souvent nécessaire d'opter pour des mesures de traitement externes. À cette fin, l'éventail des méthodes est vaste. Tout comme la méthode d'Uddeholm-Kamyr, de séparation sur résine, les techniques de traitement chimique fondées sur la précipitation à l'aide de Ca^{2+} , Mg^{2+} , Al^{3+} et Fe^{3+} peuvent maintenant s'appliquer sur une grande échelle. La méthode de Rohm et Haas, d'adsorption sur sérine, les procédés de filtration sur membranes (ultrafiltration et osmose inverse) et l'adsorption sur charbon actif ont fait l'objet d'essais sur une grande échelle tandis que certaines techniques d'écumage, d'ozonation et d'extraction aux amines ont été étudiées en laboratoire. Nous savons que ces procédés sont tous techniquement réalisables mais, il reste encore à prouver leur rentabilité économique par des essais complets et à grande échelle. D'autres techniques ont été étudiées et font encore l'objet d'études. Il s'agit de l'irradiation, de l'adsorption sur cendres volantes ou autres déchets, de l'adsorption sur alumine active, de l'épandage, d'électrolyse et de traitement biologique.

Malgré les progrès rapides nous en sommes encore aux premiers balbutiements. Nous connaissons actuellement plusieurs techniques efficaces, mais il semble qu'aucune ne s'applique à tous les effluents de l'industrie des pâtes et papiers. Les recherches devraient donc se

poursuivre afin de mettre au point d'autres types de traitement. Il reste encore beaucoup à faire en ce domaine.

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CONCLUSIONS AND RECOMMENDATIONS

1 Nature of Colour

The majority of colour in pulp and paper mill effluents is from lignin and its degradation products. In general, it is desirable to learn more about the types and characteristics of chromophores in various pulp and paper mill effluents. A more thorough understanding will lead to design of more efficient colour removal systems and also aid in determining some of their effects on the environment.

The molecular weight distribution of lignin derivatives seems to be a key factor in removal mechanisms. Further studies using gel filtration techniques could provide useful information if coupled with studies of removal mechanisms in various processes.

In any case, it is important that mechanisms of colour removal in each process be understood in addition to understanding colour characteristics.

Attempts should be made to study the efficiency of various combinations of unit processes based on an understanding of the effluent characteristics and removal mechanisms involved.

2 Effects of Colour

The effects of pulp mill effluent colour are not well known. This stems partly from the lack of understanding of the nature of this colour. Effects on the aquatic environment are largely speculative in nature and a large amount of research is needed in this area. Some of the main needs at present include:

- a) Further studies on the ultimate fate of these lignin derivatives in the environment are required.
- b) The effects on photosynthetic productivity should be studied in detail.

- c) From both a waste treatment viewpoint and for degradation in the natural environment, it would be worthwhile to investigate bacterial strains capable of rapid utilization of these macromolecules.
- d) Studies of organic colour-trace metal complexing, both in the mill and in the aquatic environment, would be extremely valuable in assessing possible harmful effects of these materials.
- e) Further evaluation of the extent of the colour problem is required, i.e., surveys of the background colour and flows of rivers as well as mill effluents; studies of perception of colour in rivers to find out what levels are detectable and objectionable.

3 Colour Measurement

Colour is measured spectrophotometrically as percent transmittance and compared to platinum-cobalt standards. There have been a wide range of conditions used to measure the colour of waste effluents and receiving waters. This has made it difficult to compare results of decolourization studies and also data collected by regulatory agencies. The best method developed to date has been described by NCASI (1971) and should be used in future studies until some other procedure is proven superior. Continuous colour measurement has not yet been achieved, but the development of such methods should be given high priority.

4 Biological Treatment

It is generally accepted that conventional biological treatment systems are relatively ineffective in removing colour from pulp and paper wastes. However, low rate activated sludge treatment can remove up to 40% under optimum conditions and fungal systems may be able to complement this removal. Further investigations are warranted to determine the

mechanism of removal. It may then be possible to increase removal to 50% to 60% so that subsequent treatment, if required, would be less costly. Also, changes in molecular weight of colour bodies during biological treatment may make them more amenable to chemical precipitation.

This may be considered optimistic by those who feel that biological treatment could be eliminated altogether and replaced by physical-chemical and other advanced treatment processes, but the biological systems already on stream would benefit from such information.

5

Lime

Lime treatment methods offer the most advanced colour removal technology in North America. However, less than half a dozen full scale facilities have been installed and not all of these are running continuously. Sludge dewatering and effluent recarbonation have been the major problems. Better equipment and development of modified treatment systems have made these processes more reliable. However, before lime treatment is tested on a large scale in Canada, it is recommended that magnesium enhanced lime treatment be evaluated in detail on a pilot scale.

6

Lime - Magnesium

A process involving excess lime precipitation of magnesium hydroxide as the principal coagulant appears to have several advantages over the lime-alone processes. There are several specific research needs relating to this approach. The most important of these are:

- a) One of the most important factors to be evaluated is the amount of colour release during sludge carbonation. This should be done at an early stage as it may be a limiting factor.

- b) Further development of magnesium recovery processes is essential to ensure the economic feasibility of magnesium coagulation.
- c) Removal mechanisms should be further elucidated by: (i) electrophoretic mobility studies of the floc particles and colour molecules, and (ii) gel filtration studies of coloured material before and after treatment.

7 Aluminum and Iron Salts

Less emphasis has been put on these methods in North America and they are not likely to become important here unless coagulant recovery techniques improve considerably. It is not recommended that small scale tests of conventional chemical processes be conducted. However, as previously mentioned, there is room for innovation. Current work at PPRIC and the Wastewater Technology Centre on alum-powdered activated carbon systems has shown potential. Also, it would be worthwhile to investigate the Japanese iron-lime process of dissolving scrap iron in the acidic chlorination stage effluent and using this as a source of FE^{2+} and FE^{3+} ions.

8 General Chemical Treatment

Treatment by chemical methods can achieve good colour removal from the total mill effluent (65% to 95%), but the residual colour is generally at least 100 (more likely 200 to 300) APHA units in the "decolourized" effluent.

In the near future, further decolourization will likely be required by law and, if not by law, by a desire to reuse effluents in the manufacturing processes. Three alternatives for accomplishing this exist: (i) chemical methods must be improved to remove this residual colour or, (ii) other unit processes must be used in conjunction with chemical

treatment or, (iii) systems not including chemical precipitation must be used.

9 Activated Carbon

Adsorption on activated carbon is capable of further removing colour from chemically treated wastes, but also leaves a colour residual that can be as low as 5 or as high as 50 APHA units. There is much developmental work being done to find effective carbons at reasonable costs. Regeneration of carbon is necessary to make this method economically feasible. Current interest in producing carbon from black liquor is worthy of further research.

More development work on activated carbon treatment should be carried out since this method has potential as a polishing stage of a multi unit colour removal system. Treatment with activated carbon appears to be most effective if preceded by lime treatment and such a system can produce a water that could be reused in many of the mill processes.

10 Resin Adsorption/Ion Exchange

Two commercial resin processes (Uddeholm-Kamyr and Rohm and Haas) have been developed to a high degree, the former to full scale and the latter to pilot scale application. They are both capable of producing a combined mill effluent similar in colour to the chemically treated processes (i.e., 100 to 200 APHA units). They both treat the first caustic extraction stage bleachery effluent and give a 95% colour reduction of this waste.

There are potential corrosion problems due to chloride buildup in these systems. It is felt that further testing must be carried out by the companies themselves. Mobile pilot scale test units are in operation by these companies and arrangements can be made for mill site trials.

11 Membrane Processes

Reverse osmosis is capable of producing an effluent of very low colour (≈ 5 APHA units) that can be reused within the pulp and paper mill. Ultrafiltration is applicable to the highly concentrated and coloured caustic extract effluent. Colour removals comparable to lime treatment (i.e., 95% from the caustic extraction stage) are obtained at relatively high flux rates.

The main needs are in developing reliable equipment. At present, short membrane life and continual fouling of equipment are hampering advancement of these processes. Large scale testing of various commercial units is underway in the U.S. This appears to be the most satisfactory approach to further research. If mechanical problems can be overcome, membrane processes (especially reverse osmosis) have a huge potential for producing recyclable water and a concentrated liquor that could yield many valuable by-products.

12 Ozonation

Ozone technology is developing rapidly. It appears to be most applicable as a tertiary method to be applied after biological treatment. Several questions are still to be answered.

At present, the systems available are expensive to install and operate, but further investigations on a large scale are recommended to determine the capacity of ozone for colour, BOD, COD and toxicity removal, as well as to generate reliable cost data.

13 Adsorptive Bubble Separation Processes

Precipitation-flotation using a metal salt along with a surfactant is not likely to be used if the metal precipitation step can successfully be eliminated from the process as in the ion flotation approach tested by researchers at the

University of British Columbia. These methods can remove over 90% of the colour from the caustic extract waste, but much work is required before a full scale system could be designed. A satisfactory recovery method for the process chemicals has not yet been developed. For economic viability a recovery technique must be developed.

14 Amine Extraction

This process is similar in principle to ion flotation giving 90% colour removal from the caustic extract stream. Problems with amine recovery have not been worked out as yet and these must be solved before advancing to large scale application.

15 Other Methods

The activated alumina treatment process is a current idea requiring detailed evaluation. This method could potentially reduce colour and toxicity concurrently (a most desirable situation).

Disposal on land is a method of advanced wastewater treatment gaining favour in some quarters at the present time. Under optimum soil conditions, good colour removals can be achieved by this method. Further evaluations appear to be worthwhile. Electrolysis and irradiation cannot be recommended for further evaluation at this time due to the expected high costs of treatment.

16 In-Plant Modifications

General methods of reducing colour loading at the source are discussed in the text. Each mill must evaluate its particular situation and apply in-plant modifications for pollution control where possible. It is difficult to test many of these methods outside the mill environment so it is largely a matter of continuing government-industry cooperation for pollution abatement research.

By-Product Recovery

Pulp and paper mill effluents contain many valuable organic and inorganic waste materials which are usually incinerated to utilize their heat value or discharged to receiving waters. Some mills are recovering useful by-products from these waste materials. A tremendous potential exists for recovery of waste by-products and such practice should be actively pursued.

1 INTRODUCTION

1.1 Scope and Objectives

In Canada the 1970 water usage by the pulp and paper industry was estimated at $3.353 \times 10^9 \text{ m}^3$ (737.6 billion Imp. Gal) or 18.5% of the national water consumption (O.E.C.D., 1973). This figure is even higher in some other countries such as Sweden and Finland where respective water consumption by the industry are 68% and 74%. This water use inevitably leads to the discharge of large volumes of wastewater generally containing significant levels of BOD, COD, suspended solids, toxicity and colour. Traditionally, wastewater treatment has involved the reduction of BOD and suspended solids and, in Canada, toxicity, with little or no emphasis on colour reduction. There appears to have been two reasons. First, colour is extremely difficult and expensive to remove and, secondly, no urgent reasons to remove colour have been identified. However, in recent years a considerable amount of effort has gone into development of colour removal techniques, prompted by a trend in the industry toward water conservation through reuse and recycling of process waters, and by an increasing public demand for surface waters that not only are free of harmful substances, but also look clean.

At the present time no particular method of colour reduction has emerged as the 'practicable technology'. However, several processes have been demonstrated on a full scale basis.

Although Canada has no full scale colour removal facilities at this time, research and development work is being conducted by government, industrial and university sectors. In order to identify future research areas for the Environmental Protection Service and the Wastewater Technology Centre, it was necessary, and is the objective of this report, to review and update not only ongoing research programs, but also the literature pertaining to colour removal technology. Several excellent reviews of the general area have been prepared previously, i.e., Gillespie and Berger (1971), Tyler and Fitzgerald (1972), Gehm (1973), Timpe (1973), Gallay (1973), Vincent (1973) and Gellman and Berger (1974). Therefore, it is not the purpose of this report to provide an exhaustive literature review, but to identify the

salient features of the problem and current research. It is also felt that work has proceeded on colour removal without the problem really being defined. An effort will be made to assemble information on colour characteristics and environmental implications of colour with the hope of aiding in understanding and defining the colour problem created by pulp and paper mill effluents.

1.2 Basic Concepts of Pulp and Paper Manufacturing

In order to appreciate the extent and type of colour problems encountered in the pulp and paper industry it is necessary to have a basic understanding of the pulp and paper manufacturing processes. Text books are available for complete details [e.g., Casey (1952), Britt (1970) and Rydholm (1965)]. Recently an excellent review manual of the basic technology of the pulp and paper industry was prepared for the Environmental Protection Service by Bruley (1974). In addition, other reports by Kleppe and Rogers (1970), Gehm (1973) and Bodenheimer and Smith (1966) provide summaries of the pulping and bleaching processes. The phases leading to a finished paper product include wood pulping, pulp bleaching and paper making. Some plants have only pulping facilities, whereas others may have pulping following by bleaching (or no bleaching) and paper making. The principle objective of wood pulping is to separate the cellulose fibres from each other for subsequent use in paper making. These fibres are bound together in wood by lignin which may be solubilized by a number of mechanical and/or chemical methods. The main pulping processes employed are mechanical or groundwood pulping; and, sulphite, neutral sulphite semi-chemical (NSSC) and kraft pulping which are collectively termed chemical pulping. The basic flow sheets for these processes are included here in Figures 1 through 4, respectively. Detailed discussion of each system is beyond the scope of this report; however, further details are provided in the aforementioned references.

Very briefly, groundwood pulping involves forcing logs into contact with a revolving grindstone in the presence of water. Lignin is softened, but not removed, so there is little colour problem with these effluents.

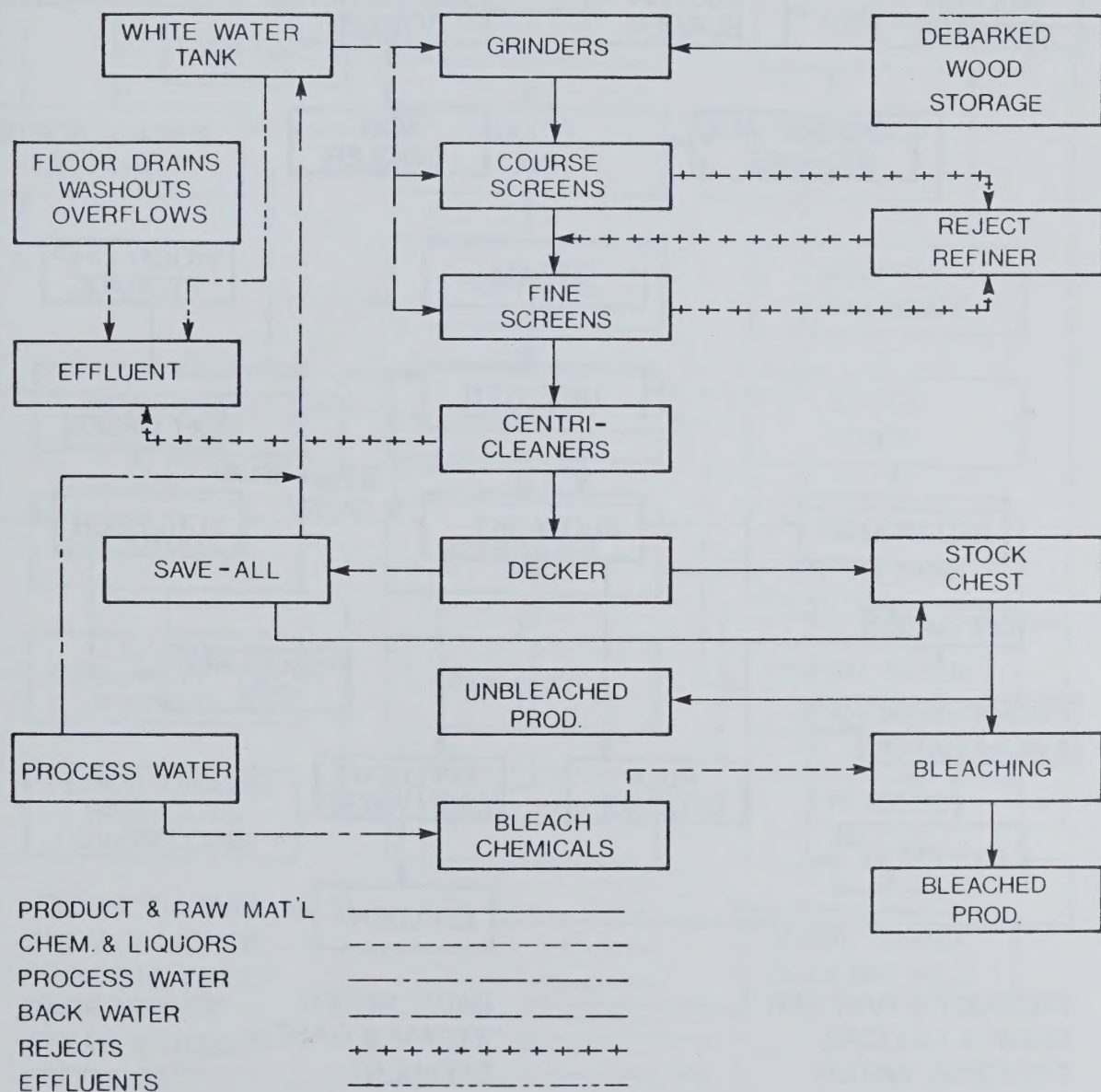


FIGURE 1. GROUNDWOOD PULPING PROCESS DIAGRAM
(GEHM, 1973)

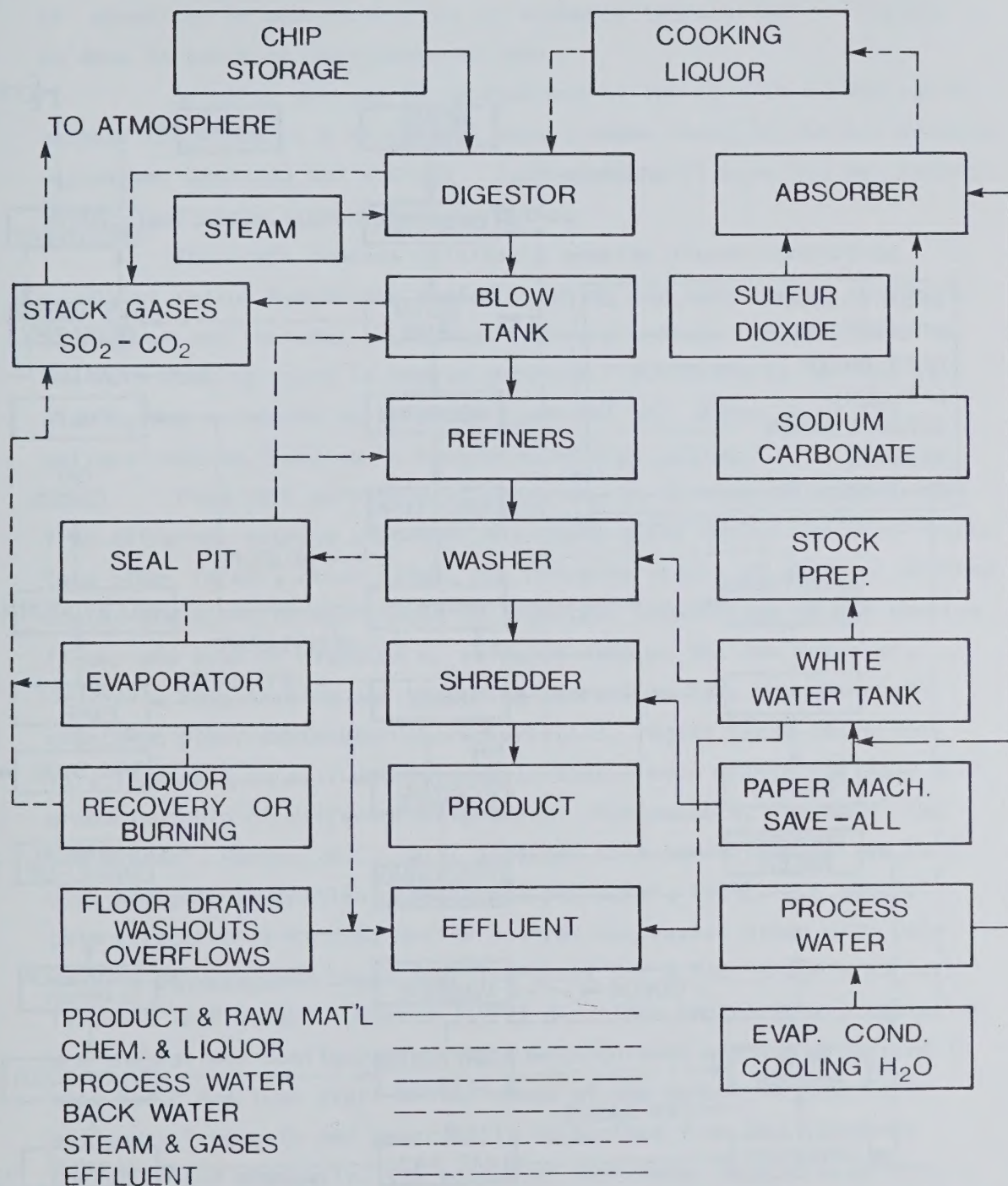
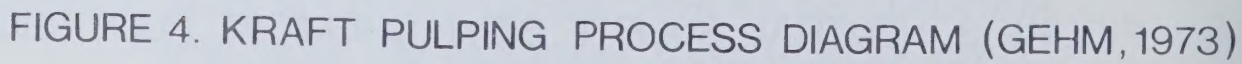


FIGURE 3. NEUTRAL SULFITE SEMI-CHEMICAL PULP PROCESS
 DIAGRAM (GEHM, 1973)



All the chemical processes involve the use of water solutions of chemicals to cook wood chips at elevated temperatures. This may be done in batch or continuous systems.

Sulphite pulping is carried out at low pH with a solution of sulphur dioxide plus a bisulphite base (common bases in use are calcium, magnesium, ammonium and sodium). Each system will have its own recoverability and waste liquor characteristics.

The kraft process utilizes a cooking liquor consisting mainly of sodium hydroxide, sodium sulphide and some sodium carbonate at high pH and includes a chemical recovery system. In NSSC pulping, the main cooking agent is sodium sulphite. Buffering is carried out with sodium carbonate to maintain a neutral pH. After about 50% delignification, pulping is completed by disc refiners.

From this very brief discussion, it is apparent that wastes from different pulping processes will have quite varied characteristics. Some other factors which affect the characteristics of chemical pulping wastes are yield to which wood is digested, composition of the cooking liquor and type of hardwood or softwood used as the raw material.

Pulp washing and bleaching operations have a pronounced effect on plant wastewater characteristics. Again these operations vary from mill to mill and in some instances even within the same mill producing pulp of different brightness. For example, the MacMillan and Bloedel, Harmac, B.C., mill produces both semi-bleached and full-bleached pulp (MacMillan and Bloedel personnel, 1974). In general, pulp bleaching is carried out in several sequential steps with pulp washing between each stage. A flow sheet for a four-stage bleachery is shown in Figure 5. Histed (1972) describes the bleachery operation and the various configurations of countercurrent washing practiced in most North American kraft mills. Much of the colour in wastewater effluents from pulp and paper mills is derived from the bleachery operation and obviously, the volume of wash water used will affect colour concentrations. Attempts are being made in most modern mills to reduce water consumption and increase water reuse. These practices lead to a reduced flow of more concentrated final effluent which facilitates external wastewater treatment. Plant modifications are discussed in a subsequent section of this report.

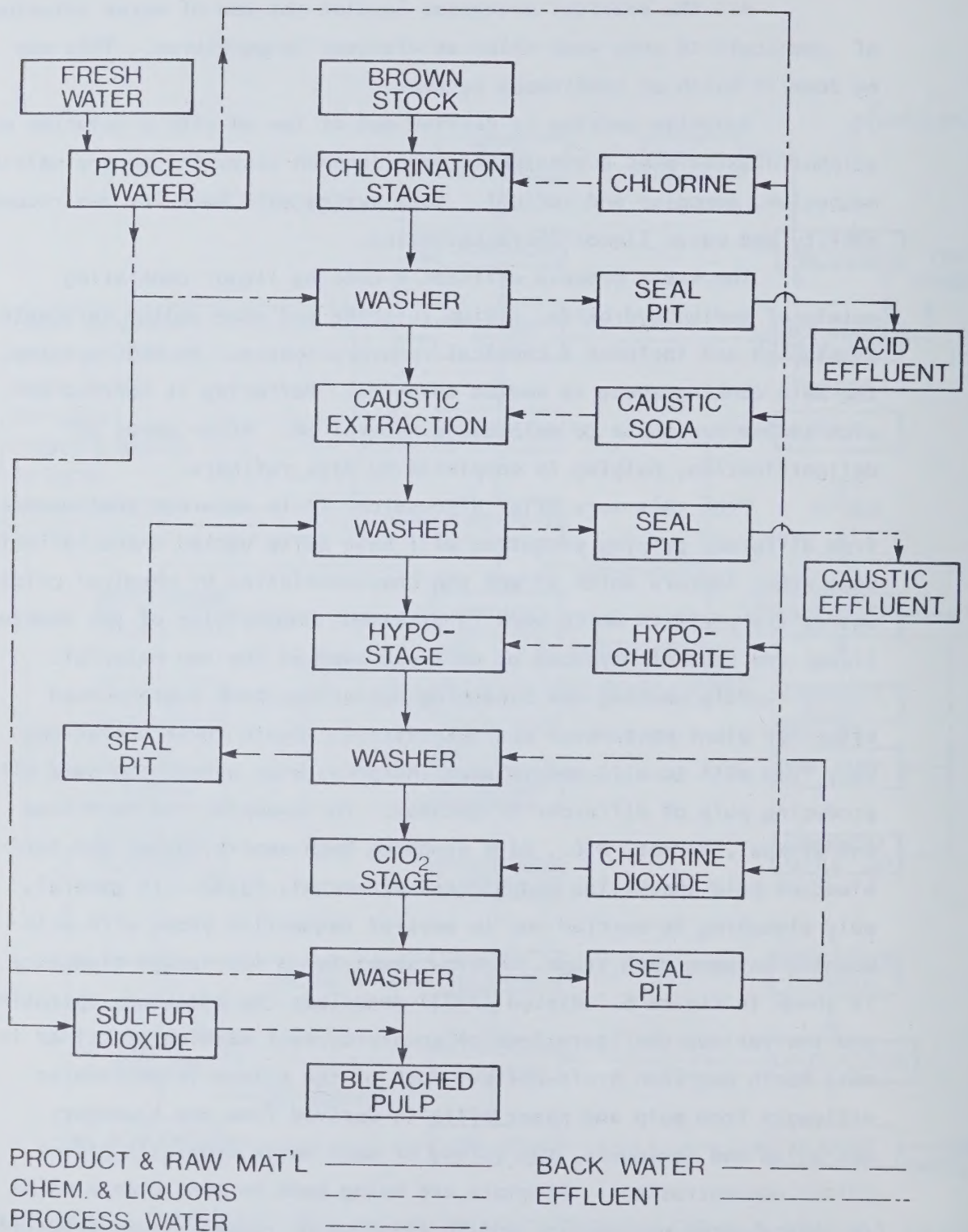


FIGURE 5. FOUR STAGE PULP BLEACHERY PROCESS
DIAGRAM (GEHM, 1973)

All mills are not integrated (i.e., produce pulp and paper); some produce only pulp, others only paper. All pulp is not bleached and considerable unbleached pulp is used to produce paper bags and cardboard. These variations make it extremely difficult to compare effluents from different mills. Even mills falling into the same general category or the same mill over a period of time may have significantly different effluent characteristics. Kleppe and Rogers (1970) have compiled data from several southern U.S., mills which can be used for general wastewater comparisons. The mill classifications are shown in Table 1 and the pollutional loads with respect to BOD, suspended solids, dissolved solids and colour are summarized in Table 2.

Bleached kraft pulp and paper mills traditionally have the highest water consumptions and the highest colour loadings. In addition kraft pulping is by far the most popular process because of its versatility and chemical recoverability. Gehm (1973) reports that 80% of the chemical pulp produced in the U.S. is turned out by the kraft process. This figure also applies in Canada (OECD, 1973). Because of its widespread usage, kraft pulping has received the most attention from a pollution standpoint.

Colour levels occurring in the process stream of kraft mills have been reported by Oswalt and Land (1973), B.C. Research (1973) and others. In general, a large percentage of the colour loading from the mills is derived from the first caustic extraction stage of the bleachery. For example, Lindberg (1973) has reported that 95% of the total bleachery colour loading in a particular kraft mill was due to the caustic bleach stage. A more general figure, based on other literature, would be in the order of 90% of the total bleachery colour or up to 70% of the total mill effluent colour. Again this figure will vary from mill to mill. Because a large portion of the colour problems in kraft mills can be attributed to the caustic extraction effluent, many colour removal investigations have centred on that stream.

The colour of various effluent streams is considered further in the next section on the nature of colour.

TABLE 1. SURVEY OF SOUTHERN PULP AND PAPER MILLS
(KLEPPE AND ROGERS, 1970): CLASSIFICATION AND WATER USE

Group of Mills	Type of Product	No. of Mills	Size of Mills (Tons of Product/Day)	Water Use (gal/ton Product)
A	Unbleached kraft pulp & paper	15	250 - 1970	20,000
B	Bleached kraft pulp & paper	5	700 - 1400	38,300
C	Unbleached & bleached kraft pulp & paper	7	160 - 1100	29,200
D	Unbleached & bleached kraft & groundwood pulp & paper	5	590 - 1465	25,800
E	NSSC & waste-based pulp & paper	1	800	24,700
F	Unbleached kraft & NSSC pulp & paper	5	727 - 2500	19,300
G	Bleached kraft & NSSC pulp & paper	1	1250	23,600
H	Unbleached & bleached kraft & NSSC pulp & paper	2	1300 - 1450	21,600
I	Unbleached kraft pulp & paper (10%)	1	860	11,200
J	Bleached pulp (highly purified)	2	570 - 1100	54,500
K	Board from waste	2	110 - 120	1,800

1.3 Nature of Colour

The concept of organic colour in natural waters and wastewaters is very complex. For decades colour removal from surface waters has been a concern in water treatment. Black and Christman (1963), Hall (1970) and others have reviewed much of the significant research in this area.

The colour in pulp and paper mill effluents can be expected to have unique properties resulting from the chemical reactions during pulping and bleaching. However, many of the observations and research techniques of water chemists provide excellent background information

TABLE 2. POLLUTION LOAD IN RAW WASTEWATER FROM THE DIFFERENT TYPES OF SURVEYED MILLS (KLEPPE & ROGERS, 1970)

Groups of Mills ²	Amount of Wastewater (gal/ton of product)	BOD (lb/ton of product)	Suspended Solids (lb/ton of product)	Dissolved Solids (lb/ton of product)	Colour ¹ (lb/ton of product)
A	10,900-27,800 Ave. 18,500	19.5-69.5 (12) Ave. 43.0	10-99 (10) Ave. 37.5	84-200 (4)	250 (1)
B	24,400-56,000 Ave. 38,000	46-128 (5) Ave. 78.5	93-460 (5) Ave. 205	325-540 (3)	300-390 (3)
C	31,000-90,000 Ave. 37,000	54.5-84.0 (6) Ave. 67.0	61-226 (5) Ave. 100	365 (1)	435 (1)
D	19,000-26,000 Ave. 23,200	30.1-59.0 (5) Ave. 44	90-150	190-250 (3)	100-175 (2)
E	6,000	26.5 (1)	-	-	-
F	15,000-22,000 Ave. 18,600	20-47.5 (5) Ave. 35	32-49 (5) Ave. 43	28-115 (2)	160-175 (2)
G	21,600	54.0	108.0	460	375
H	21,800-28,300	30.5-50.0	73 (1)	225-235	305 (1)
I	13,400	44.0	56.0	112	-
J	52,500-79,000	108-140	210 (1)	750-980 (2)	-
	0-750	0-7.5	0-12.5	0.14	-

() Number of mills included.

¹ Based on platinum equivalents in cobalt chloroplatinate (colour units), and expressed as lbs/ton.

² Classifications of the mills are given in Table 1.

for investigations of pulp and paper mill colour characteristics. Colour values encountered in mill wastes are generally several orders of magnitude higher than surface water values.

Typical colour values for some pulp and paper effluents and other substances of general interest have been given by Tyler and Fitzgerald (1972) as follows:

Bleached kraft mill effluent	2,000 APHA Units
Caustic extract	20,000 APHA Units
Unbleached kraft mill effluent	700 APHA Units
Magnesium base sulphite effluent	5,000 APHA Units
Coffee	10,000 to 15,000 APHA Units
Coca-Cola	8,500 APHA Units
Draft beer	1,000 APHA Units
Northern Canadian waters	100-200 APHA Units

Results of a study by B.C. Research (1973) of colour levels in nine B.C., kraft mills (shown in Table 3) more or less confirm these generalizations and also show the large fluctuation in colour of the same effluent stream. Similar inventories of mill process colour loads and sources should be conducted at other mills to get a clearer picture of the colour contribution of various effluents.

It is generally accepted that almost all the colour of these effluents is due to lignin or lignin derivatives (Hartler and Norrstrom, 1969, and Swanson et al, 1973). However, the particular method of wood pulping and pulp bleaching employed will determine the characteristics of the effluent and the nature of the chromophores (colour producing structures) present.

Fundamental research has been going on in the field of lignin chemistry for more than 100 years, but only recently has the structure of the lignin molecule been fairly well elucidated. Although a precise definition of lignin is difficult it can be tentatively described as a highly branched or cross-linked, highly reactive polymer with a sub-unit of molecular weight of about 840. Several reviews of lignin chemistry have been compiled, e.g., Sarkanen and Ludwig (1971) and Marton (1966). Parts of these two references are devoted to the reactions involved in

chemical pulping and bleaching processes. In addition, works by Gierer (1970), Gierer et al (1973), and Bodenheimer and Smith (1966) provide further details on pulping and bleaching reactions.

TABLE 3. COLOUR LEVELS* OF VARIOUS PROCESS SEWERS AND COMBINED OUTFALLS FOR NINE B.C. BLEACHED KRAFT MILLS (B.C. RESEARCH, 1973)

Mill	COLOUR IN EFFLUENT STREAM IN APHA UNITS			
	Unbleached White Water	Caustic Bleach	Acid Bleach	Whole Mill Outfall
A	1248 ± 530	11430 ± 1747	646 ± 148	3664 ± 1293
B	3504 ± 1565	9472 ± 2380	854 ± 185	2544 ± 708
C	1464 ± 601	5484 ± 3125	617 ± 105	3668 ± 886
D	3724 ± 1101	4448 ± 1197	1121 ± 449	2600 ± 670
E	782 ± 319	7376 ± 1857	678 ± 249	2308 ± 420
F	1359 ± 1119	9254 ± 1236	1121 ± 449	1192 ± 299
G	966 ± 504	9420 ± 2692	868 ± 365	-
H	2664 ± 943	16964 ± 3301	2341 ± 1210	2160 ± 872
I	1707 ± 636	22780 ± 5925	1600 ± 693	2222 ± 511

* Values expressed as means and standard deviations, representing 10 sampling dates.

During pulping, natural lignin of wood is dissolved by appropriate chemicals in preparation for subsequent separation from the wood fibres during pulp bleaching. Important reactions in these processes include sulphonation, sulphidization and hydrolysis in pulping and halogenation and oxidation in bleaching. These reactions result in various structural units which give rise to effluent colour. Although a great deal of effort has been aimed at identifying the specific chromophoric groups responsible for colour, the matter has not been completely resolved. Most of the research to date has dealt with kraft effluents since this is the predominant pulping process in use. Kraft pulping gives rise to thiolignin and alkali lignin whereas sulphite pulping results in liginosulphonic acid or precipitated liginosulphonate.

It is recognized that reactions in the bleach plant further degrade the products of the pulping operation so that the bleach plant effluents contain a combination of pre-existing chromophores and some additional, possibly different, chromophoric groups created by the bleaching process itself. Falkehag et al (1966) have summarized the major chromophoric systems in kraft lignin as: $\text{CH} = \text{CH}$ double bonds conjugated with the aromatic ring and quinonemethides and quinones which may also serve as oxidative species creating further chromophoric structures; minor systems included chalcone structures, free radicals and metal complexes with catechol structures. It is assumed that a composite series of chromophore systems are present in these effluents.

Subsequent studies by NCASI Bulletin #239 and #242 (1970), Meshitsuka and Nakano (1973) and others have provided more specific information that confirm these generalizations. In particular *o*- and *p*- benzoquinone are found to be important intermediate coloured structures formed in bleaching and the presence of metals, particularly iron, has been shown by the latter authors to contribute to the colour of lignin degradation products. Complexing of iron with organic molecules was also reported in NCASI Bulletin #273 (1973) but insufficient work has been done on this to determine the role of metals in colour formation.

One of the most important characteristics of lignins and their degradation products is their polydisperse nature (exist over a wide range of molecular weights). Molecular weight distributions of pulp mill effluents have been studied using gel filtration techniques as reviewed and described by Obiaga and Ganczarczyk (1972) and others. An example of a molecular weight distribution for alkali lignin is shown in Figure 6. Varying distributions have been found for different effluents; however, all have demonstrated polydispersity. In general, molecular weights in kraft pulp mill effluents seem to be lower than in sulphite liquors and these pulping effluents contain more high molecular weight coloured compounds than do bleaching effluents because of the further degradation occurring during bleaching. Typically a combined mill effluent may contain materials with molecular weights of less than 400 up to 150,000.

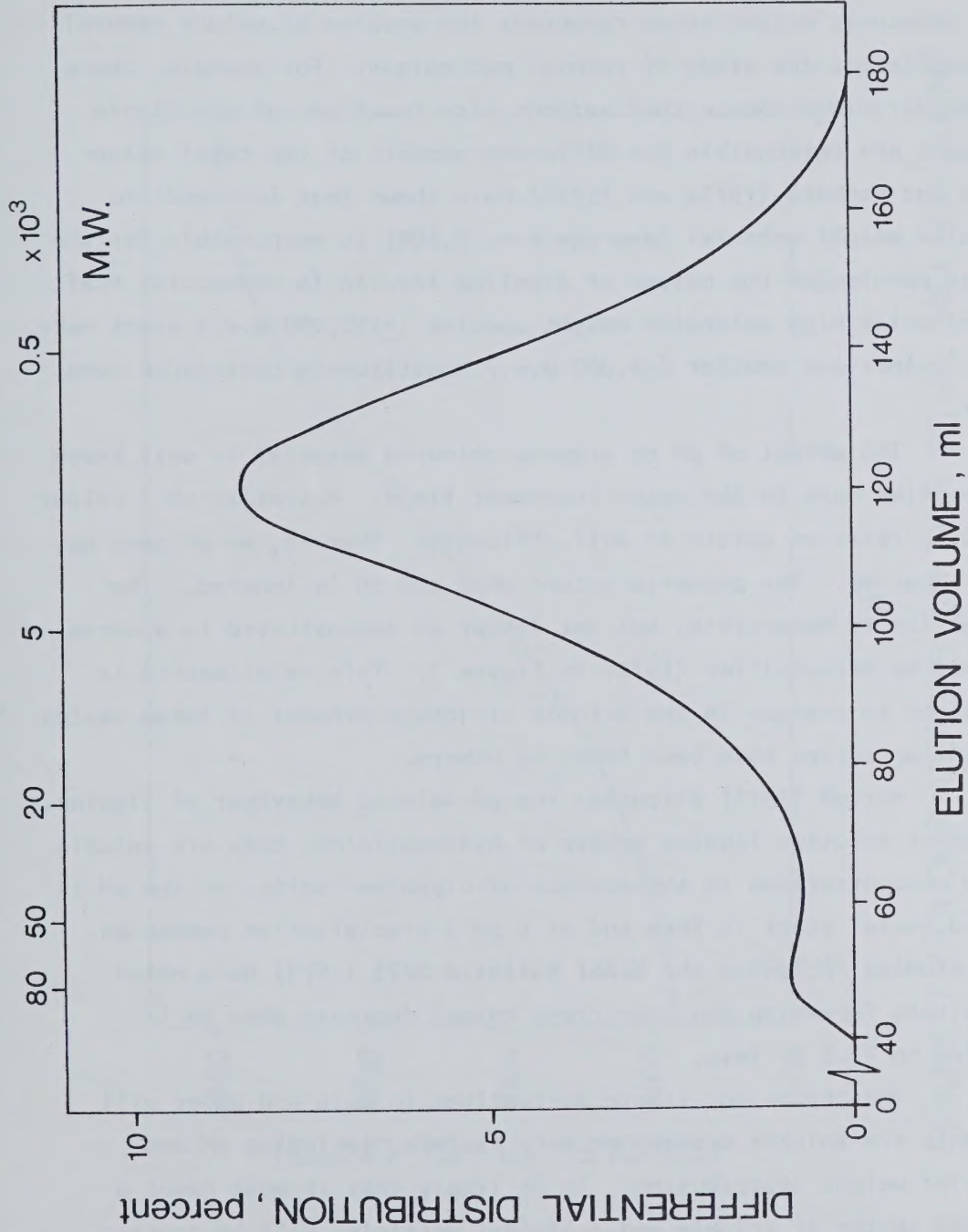


FIGURE 6. TYPICAL MOLECULAR WEIGHT DISTRIBUTION OF ALKALI LIGNIN OF SIMULATED KRAFT PULP MILL WASTEWATER (GANCZARCZYK AND OBIAGA, 1974)

Further information on the polydisperse nature is provided in papers by Shotton et al (1972), McNaughton et al (1967), Pew and Connors (1971), Collins et al (1969) and (1971), and Soundararajan and Wayman (1970). The fact that the coloured materials exist over a broad molecular weight range compounds the problem of colour removal and complicates the study of removal mechanisms. For example, there is considerable evidence that various size fractions of the lignin compounds are responsible for different amounts of the total colour. Rankin and Benedek (1973a and 1973b) have shown that intermediate molecular weight material (average m.w. 5,600) is responsible for the largest portion of the colour of alkaline Indulin (a commercial kraft lignin) while high molecular weight species ($\geq 150,000$ m.w.) exert very little colour and smaller ($\leq 4,000$ m.w.) constituents contribute some colour.

The effect of pH on organic coloured material is well known from earlier work in the water treatment field. A similar pH - colour intensity relation exists in mill effluents. That is, as pH goes up, colour goes up. The converse occurs when the pH is lowered. The interaction is reversible, but not linear as demonstrated in a curve obtained by Herschmiller (1972) in Figure 7. This relationship is attributed to changes in the quinoid structure present in these wastes and similar curves have been found by others.

Marton (1971) discusses the pH related behaviour of lignins. In aqueous solution lignins behave as hydrocolloids; they are soluble at low concentrations in the absence of dissolved salts; as the pH is lowered nuclei start to form and at a pH 3 precipitation commences. Other studies including the NCASI Bulletin #273 (1973) have noted precipitate formation and concurrent colour decrease when pH is adjusted to ≤ 2.5 or less.

Whether or not lignin derivatives in pulp and paper mill effluents are soluble depends on many factors, including pH and molecular weight distribution. It is likely that in most cases a combined system of soluble and colloidal particles will be present. However, those in alkaline kraft mill effluent are generally considered to be soluble while in sulphite liquor there appears to be two fractions

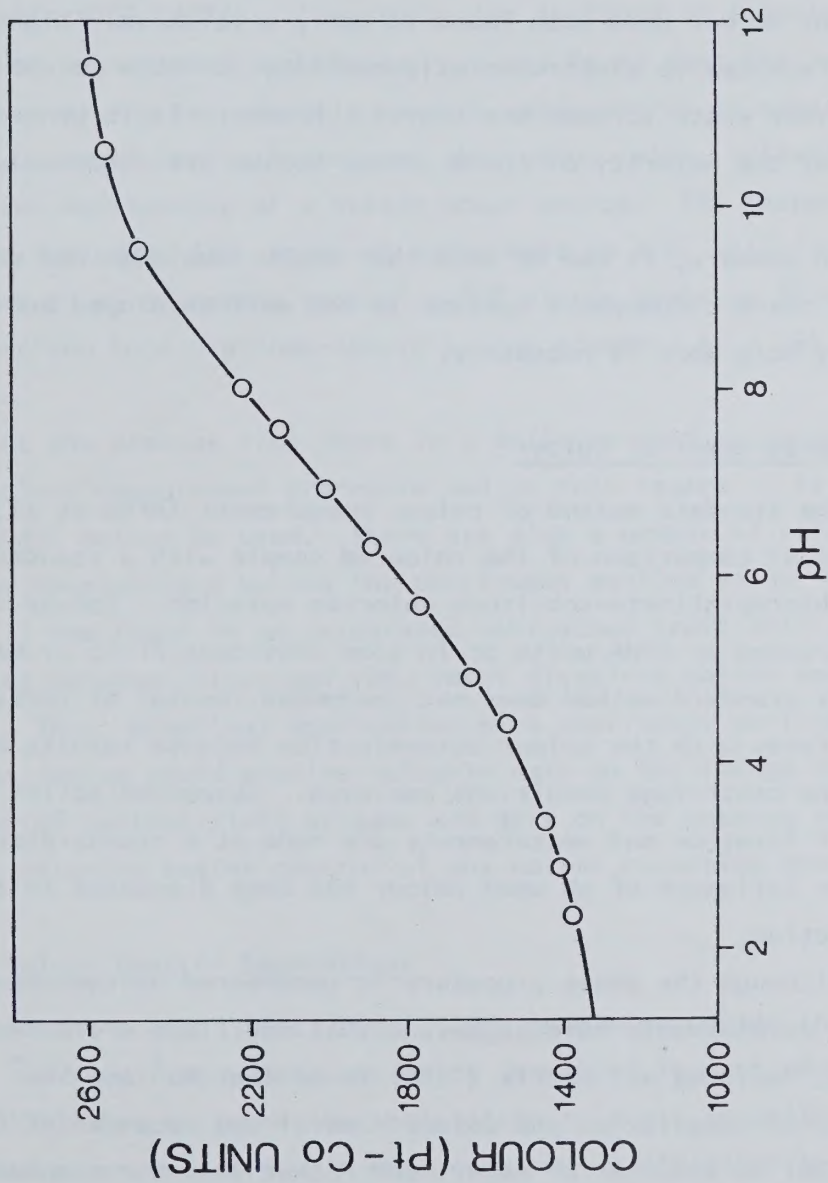


FIGURE 7. COLOUR VERSUS pH FOR TOTAL MILL EFFLUENT
(HERSCHMILLER 1972)

of lignosulphonates. These are termed α and β fractions where the α fraction has high molecular weights generally considered to be colloidal and the β fraction has small molecular weights usually thought of as truly soluble, (Pilinskaya et al, 1973).

Another factor which could have particular interest in colour removal is the electrical charge on the colour particles. According to Swanson et al (1973), all fractions of unbleached kraft mill effluent colour have been found to carry a relatively high negative charge. References to electrophoretic mobility (or zeta potential) of colour in other waste streams are scarce. However, it is generally accepted that the majority of these colour bodies are negatively charged.

In summary, it can be said that basic knowledge and understanding of these chromophore systems is not well developed and considerably more work is necessary.

1.4 Measurement of Colour

The standard method of colour measurement (APHA et al, 1971) involves visual comparison of the coloured sample with a standard potassium chloroplatinate-cobaltous chloride solution. Colour is usually expressed as APHA units or in some instances Pt-Co or Hazen units. This standard method does not recommend removal of turbidity which interferes with the colour determination because results may vary with the centrifuge conditions employed. Suspended solids are removed by filtration and measurements are made at a standardized pH of 7.6. The influence of pH upon colour has been discussed in the previous section.

Although the above procedure is considered as the standard, some recent developments have suggested that revisions are necessary. For example, Maulding and Harris (1968) found that Na^+ and $\text{SO}_4^{=}$ ions interfered with coagulation and colour removal and recommended that Ca(OH)_2 or HCl be used for pH adjustment rather than the standard chemicals, NaOH and H_2SO_4 .

Another study (NCASI Bulletin #253, 1971) revealed that the filter aids used in the Standard Methods may contribute to sample

turbidity thus giving erroneously high colour values. Lee et al (1971) suggests that a copper-cobalt-riboflavin standard is more representative of the colour and hue of kraft mill effluents. Numerous other variations on colour measurement are reported in the literature.

To date, the most extensive evaluation of colour measurement technique for pulp and paper mill effluents has been described in the NCASI Bulletin #253 (1971). The study also included an interlaboratory comparison of measurement techniques. It was found that the important factors in obtaining reproducible results were control of sample pH and clarity, use of optically matched absorption cells, reliable standards and maintenance of a stable power source. The method recommended included: (i) sample pH adjustment to 7.6, (ii) filtration of less than 50 ml of sample through a 0.8 micron membrane filter, and (iii) comparison to a platinum-cobalt colour standard at a 465 mμ wavelength.

At the present time there is a definite need to adopt a standard colour measurement procedure and in this regard it is recommended that the NCASI method be used. There are also a number of valid reasons for developing a method for continuous on-line colour measurement. South (1971) has found in an integrated unbleached kraft mill good correlations between colour and BOD, total dissolved solids and conductivity. Thus, practical application of a continuous on-line colour measurement device could provide valuable data on the change in the BOD content of various plant streams and data on the washing efficiencies etc., plus allowing better control of any colour reduction process.

1.5 Colour Control Regulations

At the present time, regulations governing colour in both effluents and receiving waters are being developed in most countries. The OECD (1973) has surveyed the legislation relevant to pollution by the pulp and paper industry. In most countries legislation pertains to BOD and suspended solids removal requirements. At the time of the OECD study, no country had specific requirements for colour removal per se, although Japan, Switzerland and Germany had a KMnO_4 demand requirement.

In some particularly sensitive locations where colour in the receiving stream is deemed aesthetically displeasing or otherwise unacceptable, local regulatory agencies often take the initiative and require not only removal of BOD and suspended solids, but also colour. There are several locations in the southeastern United States and in British Columbia in Canada, which fit into this category. As the effects of colour on receiving streams become better documented, it may be necessary to require colour removal on mill effluents on a much wider scale than is presently practiced. Interestingly enough, the recent U.S., Environmental Protection Agency (Vogt 1974) effluent guidelines for the pulp and paper industry do require colour limitations by 1983.

While it can be said that laws requiring colour removal from pulp and paper mill wastes have not been developed to the point of application in most countries, there is increasing pressure on the industry to include colour reduction in waste treatment. The action taken by the EPA in the U.S., indicates that the problem of colour in receiving streams is now being viewed as a serious one and stiffer control laws can be expected. However, it is still not exactly clear what this concern about colour is based upon. Until certain questions relating to the effects of this colour on receiving waters, and how widespread the problem is, are answered, it seems unlikely that rational standards and criteria can be developed. This will be discussed in more detail in the following section.

1.6 Effects of Colour on Receiving Waters

The reason usually given for colour removal from pulp and paper mill effluents is that receiving water colouration is aesthetically objectionable. Another much cited effect of colour is that it causes problems at downstream water treatment plants. A report by the AWWA (1970) listed the disadvantages of a coloured water supply as follows:

- (i) aesthetically displeasing;
- (ii) potential contribution to a taste problem;
- (iii) increased chlorination demand;

- (iv) potential algae or bacterial nutrient;
- (v) may foul ion exchange resins in industrial water conditioning systems;
- (vi) may interfere with certain colourmetric water analyses;
- (vii) may reduce productivity of natural waters by limiting light transmittance;
- (viii) may interfere with coagulation processes; and
- (ix) may increase concentration and stability of iron, manganese or other metals in water via chelation.

In general, there are little concrete data to substantiate the potential effects listed above and further studies are required in order to quantify the effects of coloured effluents upon receiving waters. A few pertinent studies are reviewed in the remainder of this section.

Bouvang and Lundstedt (1966) and (1968), and Hedburg et al (1968) have studied the coagulant requirements for producing potable water from surface water affected by kraft and sulphite mill effluents. They found that both effluents caused increased coagulant (alum and activated silica) requirements with the sulphite effects being more pronounced than kraft.

An extensive study of lignosulphonate buildup in a large Finnish lake by Priha (1971) confirmed these findings. The results of the study showed that when the lignosulphonate content is moderate (3 to 5 mg/l) lake water can be purified into satisfactory drinking water with conventional methods. When the concentration increases, the necessary amount of chemicals also increases, and a point is finally reached when satisfactory drinking water cannot be obtained even with increased chemical dosage.

While there is no direct evidence linking colour per se and toxicity, it is interesting to note that Betts et al (1971) identified catechol, a chromophore, as present in toxic effluents, but not present in non-toxic effluents. Das et al (1969) identified tetrachloro-o-benzoquinone, another chromophore, as the main toxic substance of a kraft bleachery effluent. These findings must be interpreted with caution because of the chemical complexity and variability of mill effluents. In fact, the assumption has been that colour is not toxic.

This stems from the observation that toxicity can be removed by certain methods that do not reduce colour concurrently. It should be pointed out that toxicity in these tests is usually defined in the context of number of fish surviving a specific concentration of effluent for a specified number of hours. Long term effects of high concentrations of colour on fish and smaller aquatic life are unknown and to date have not been studied. Aside from direct toxicity, other effects on aquatic life can only be speculated upon at this time. For example, the capacity for trace metals to complex with certain organic compounds is well known and has been shown to occur in mill effluents as mentioned previously. Accumulation of increasing amounts of these materials may have detrimental effects on aquatic populations since these materials are often more readily available to living organisms than are elemental forms of metals. Thus, addition of coloured organic materials could have an indirect toxic effect.

Also, light reduction could have several effects on the aquatic environment. According to Strickland (1958), light acts as one of the stimuli affecting grazing habits of zooplankton, and assists fish and other marine organisms in discriminatory feeding. It is likely then, that aquatic species relying on sight to locate food will have a more difficult time surviving in waters darkened by pulp mill effluents. This may lead to shifts in aquatic populations and generally disrupt the aquatic eco-system. An article by Gubitz (1966) is worth mentioning also. This author states that "trout avoid not only heavy concentrations of suspended solids, but also coloured wastewaters; and in particular, red coloured wastewaters cause fish to retreat".

Another possible consequence of light reduction is the interference this may cause in the degradation of such compounds as pesticides such as aldrin which is broken down by photo isomerization. This may or may not be beneficial since often degradation products are more toxic than their parent materials. It is interesting to note that the colour of mill effluent may hinder its own degradation in the same way since Kroner and Moore (1954) point out that sunlight enhanced the degradation of lignin.

Of obvious concern is the possibility of decreased light penetration causing a reduction of primary productivity, the basis of the entire aquatic food chain. A number of papers including one by Jones (1966) describe the relation between light intensity and growth rate of algae. However, surprisingly little work has been done to determine what effect, if any, pulp mill colour has on photosynthesis by phytoplankton.

Parker et al (1972) have studied the impact of a pulp mill effluent upon Alberni Inlet in British Columbia. They could not establish a direct relationship between oxygen deficiencies in the inlet and the oxygen demand of the mill effluent. However, they attributed the oxygen deficient condition immediately below the halocline to a failure of the photosynthetic system rising from reduced light penetration. The reduced light penetration was attributed to coloured material in the mill effluent.

B.C. Research and the Pacific Environmental Institute are currently studying the effects of colour on photosynthetic productivity, but results were not available at the time of printing.

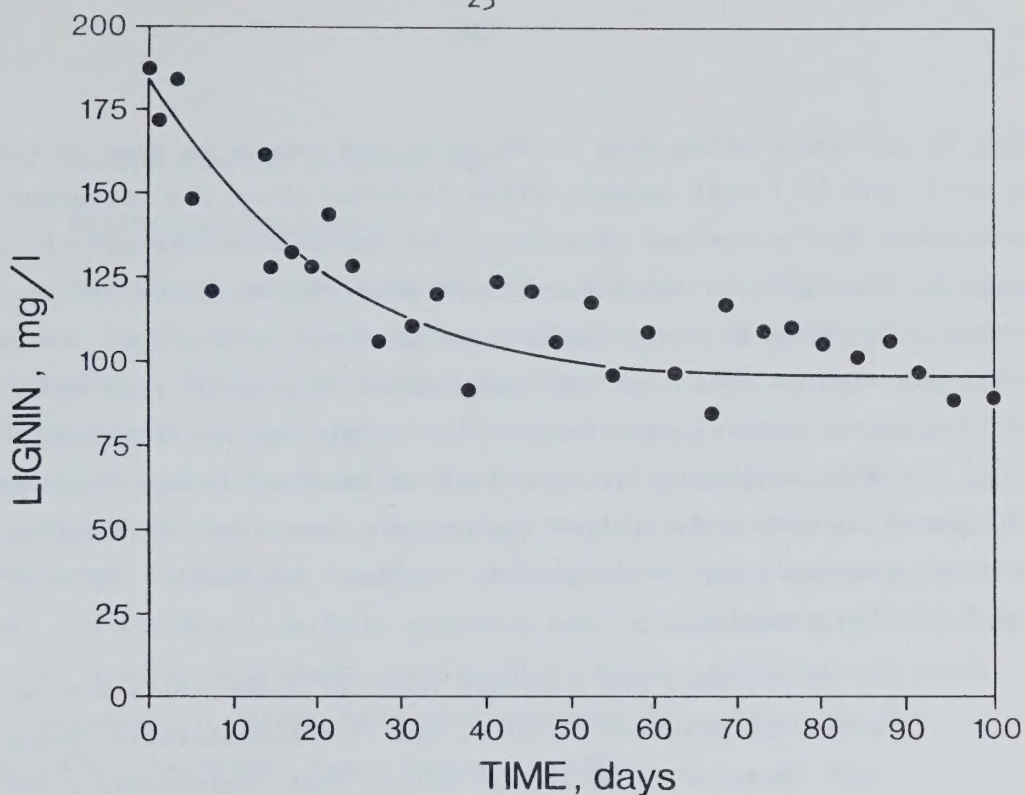
It is repeated throughout the literature that lignin derived colour bodies are biologically stable and are, therefore, unaffected by conventional biological treatment systems. This generalization requires clarification for there are researchers who feel that modified biological systems are capable of achieving a significant degree of colour removal (e.g., Ganczarczyk and Obiaga, 1974, and Nova Scotia Research Foundation, 1974). Some work has been carried out to determine the extent of lignin degradation and the long term BOD exerted on a receiving stream. Both Kroner and Moore (1954) and Raabe (1968) discussed lignin degradation and concluded that: (i) there are micro-organisms which are capable of degrading lignin, and (ii) degradation is slow and usually incomplete. Kroner and Moore (1954) studied the persistence of colour concentrations (10 ppm) of kraft lignin in water under various conditions. They found that 41% to 46% of the lignin remained after 20 days of aerobic, daylight degradation conditions. They also determined that exposure to sunlight and the presence of algae enhanced decomposition.

Raabe (1968) provided evidence that lignin degradation does occur in river waters and this degradation does exert a long term oxygen demand. The degradation of lignin over a 100-day period is shown in Figure 8a. The degradation was slow with 51.6% of the original lignin compounds still present after 100 days. The effect of lignin degradation on the long term BOD is shown in Figure 8b. The data suggest that the 5 to 20-day BOD is related to the carbohydrate content of the kraft mill effluent whereas the long term BOD is largely due to lignin decomposition. More recent data from a study by Bouveng and Solyom (1973) confirmed Raabe's (1968) work, (i.e., that pulp mill effluents contain a readily degradable organic fraction and a slowly degradable fraction). They found that unbleached kraft mill effluents contain a higher portion of the readily degradable fraction than bleached kraft effluents.

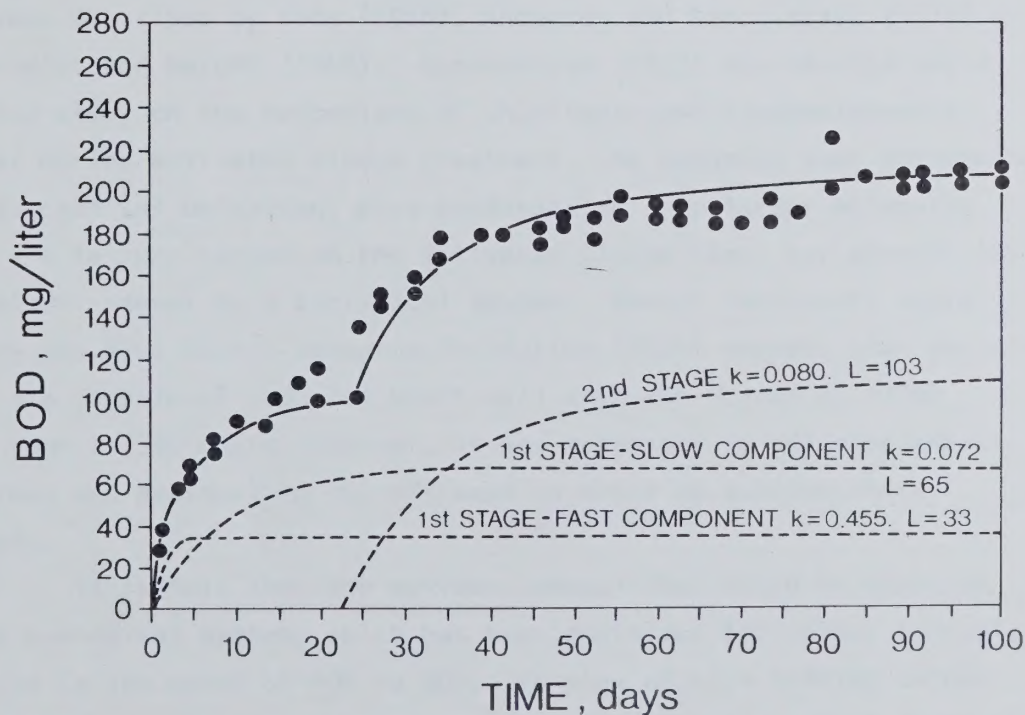
Priha (1971) points out that degradation of lignosulphonates is extremely slow and even when coupled with natural flow through a water system, input often exceeds output. For example, a buildup of these pollutants was observed in a lake where they exhibited stratification and seasonal concentration variations.

The speeding up of biochemical decomposition is impossible at present. The most important considerations in this respect would be to ensure a good supply of oxygen in the water (since most lignin decomposers are aerobes), and perhaps develop bacterial strains capable of more efficiently decomposing lignin derived compounds.

Regarding the aesthetically displeasing appearance of coloured effluents there are several questions which must be answered before rational colour removal standards can be developed. These have recently been reviewed by Gellman and Berger (1974): (i) what level of colour is displeasing (or conversely how much colour should be allowed into a stream)? This will relate to the background colour naturally present in the receiving stream and to river flows since it is dilution dependent. Some natural surface waters are already highly coloured. Before any conclusions are reached about the widespread nature of the pulp mill colour problem, it is necessary to conduct a national examination of existing background water colour and seasonal hydrological data.



8a. DEGRADATION OF LIGNIN OVER 100 DAY PERIOD



8b. LONG-TERM BOD OVER 100 DAY PERIOD

FIGURE 8. DEGRADATION OF KRAFT MILL EFFLUENT
IN RIVER WATER (RAABE 1968)

This is currently being done in the U.S. and should be done in Canada as well, and (ii) what concentration increase above the background is detectable by the average observer under various conditions? A complex study by the NCASI in the U.S., is currently trying to determine this over a wide range of environmental and personal conditions. It is ambitious studies like this that are needed to provide some basis for setting colour removal requirements for merely aesthetic reasons.

When aesthetically detectable colour levels are known and background colours and dilution factors are known for different areas, rational standards can be developed. Gellman and Berger (1974) offer the following example:

"If an effluent has a colour level of 1,000 units and receives a minimum dilution of 50:1, and if the detectable change at that location is 50 colour units, then conceivably a further increase in colour load of 150 percent would remain undetectable."

2 COLOUR REMOVAL ALTERNATIVES

2.1 Biological Treatment

It is well established that conventional biological treatment systems are ineffective in the removal of colour from pulp and paper mill effluents. Timpe (1973) concluded that up to 30% colour removal could be achieved by conventional activated sludge, whereas other biological processes (such as aerated lagoons) generally achieved less than a 10% colour reduction. Recently, Chen et al (1974) evaluated four different biological treatment methods for a pulp and paper mill effluent and found all methods achieved poor colour removals. In some biological treatment systems, particularly waste stabilization ponds, slight increases in colour have been observed (e.g., Bouveng and Solyom, 1973, Interstate Paper Company, 1971).

Some researchers have investigated modified biological systems which are capable of achieving colour removals up to 40% at low aeration tank BOD loadings (i.e., $<1500 \text{ g/day} \cdot \text{m}^3$). These studies have been described by Edde (1968), Anderson and Ganczarczyk (1971) and Schmidt and Weight (1968). Ganczarczyk (1973) has carried out a detailed study on the mechanisms of thioglignin and lignosulphonate removal during activated sludge treatment. He suggests that phenomenon such as chemical oxidation, plus condensation into larger molecules which are in turn sorbed on the activated sludge floc, may account for the colour removal by a biological system. Recent laboratory scale work by the Nova Scotia Research Foundation (1974) reveals that certain fungi are capable of reducing kraft mill effluent colour of ≈ 1800 units down to 550 units. However, it was necessary to add supplements (dextrose and peptone) to the effluent in order to achieve these removals.

It is felt that the maximum removal that could be expected from a biological system, which has been optimized for colour removal, would be in the order of 40% to 50%. In view of this limited colour removal efficiency, it has been necessary to consider various physical-chemical processes which are capable of higher degrees of removal. These processes are reviewed in subsequent sections.

2.2 Chemical Treatment

Colour removal from municipal water supplies has been carried out by chemical treatment for decades. Traditional chemical coagulants include lime and salts of ferrous, ferric and aluminum ions. Early attempts at removing colour from pulp and paper mill effluents utilized existing water treatment technology. Detailed reports on the development of chemical treatment technology for the pulp and paper industry have been prepared by Gallay (1973), Gehm (1973), Tyler and Fitzgerald (1972) and Timpe (1973). This report will review the most recent findings and the salient features of previous studies.

Iron and aluminum based precipitants have been employed more extensively in Europe, U.S.S.R., and Japan. Since lime is used extensively in kraft pulping operations, the lime approach to colour removal has gained considerable favour, particularly in the United States. There is a great deal of work currently being carried out on variations of the lime process and considerable literature already published. Consequently, lime treatment will be dealt with in separate sections.

2.2.1 Iron and aluminum salts

The mechanisms of colour removal in water treatment have been described by the AWWA (1970). Clarke and Davis (1969) and Smith and Christman (1969) specifically discuss the mechanisms involved in removing colour from pulp mill effluents with iron and aluminum.

Noteworthy work in North America involving the use of alum for colour removal has been carried out and patented by Fuller (1969), (1970), (1971) and (1973). According to Gellman and Berger (1974), the process will soon be evaluated on a full scale. A schematic of the essential features of the system is shown in Figure 9. The process is claimed to have superior BOD and colour removal efficiencies to other precipitation (iron and lime) systems. In addition, the alum will be recovered for eventual recycle.

Full scale alum colour removal studies have been carried out at the Weyerhaeuser of Canada Ltd., mill in B.C., (Hague, 1974).

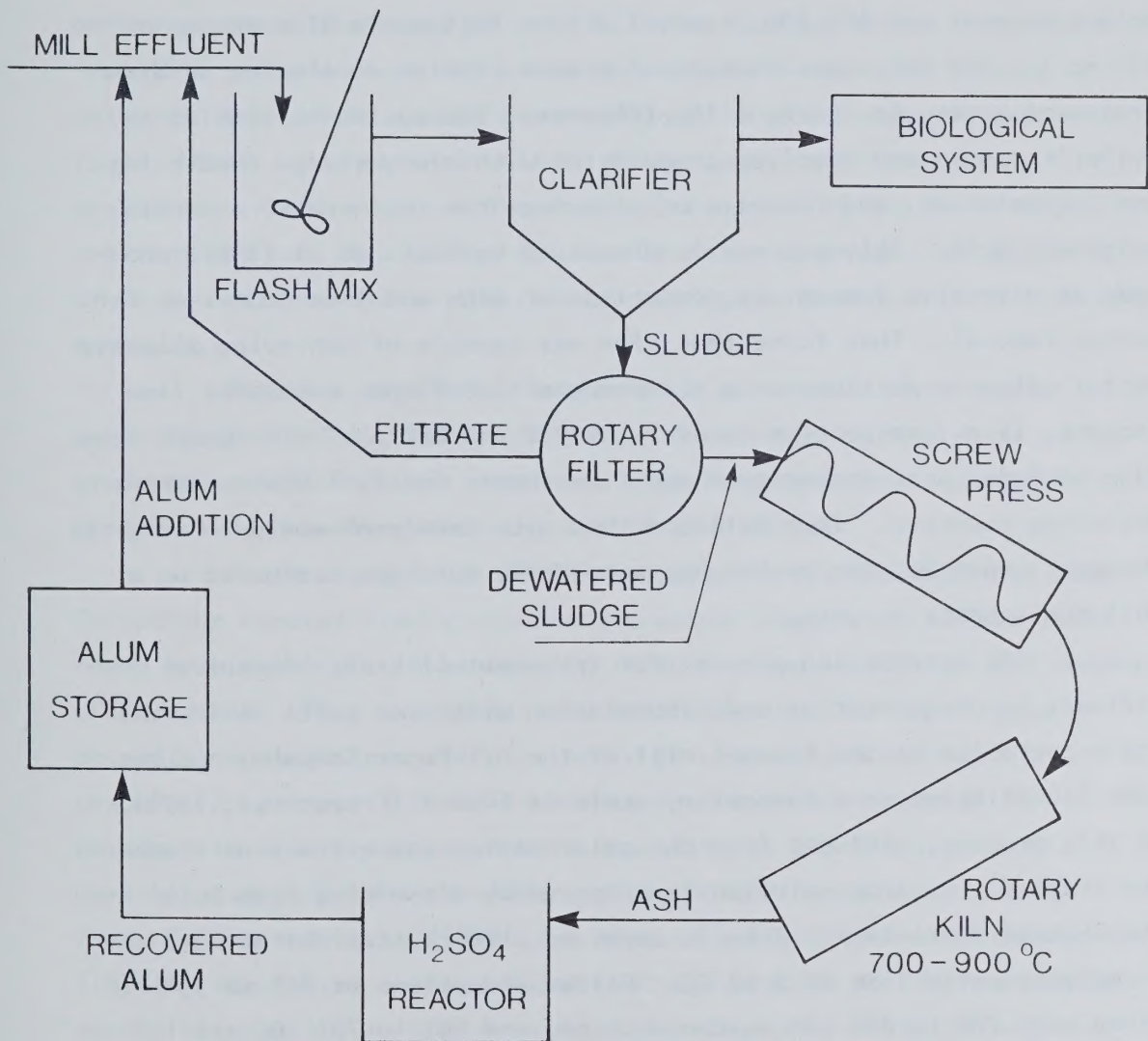


FIGURE 9. ALUM COLOUR REMOVAL PROCESS (FULLER, 1973)

During these trials numerous problems in process control were encountered. In addition, the Pulp and Paper Research Institute of Canada (Wong, 1974) is presently conducting alum, powdered activated carbon and polyelectrolyte bench scale evaluations. Freyschuss (1974) reports that one unbleached kraft mill in Sweden is presently achieving 90% colour removal and 65% BOD₇ removal with a full scale alum dosage of 120 mg/l. The Degremont Company of France is also developing an alum treatment system for kraft mill effluents. The system is similar to Fuller's system and involves coagulation with alum, sludge dewatering and incineration, and recovery of alum from the incinerated ash with sulphuric acid. This process is discussed by Bebin et al (1971) who made an extensive laboratory comparison of alum and lime processes for colour removal. They found that alum was capable of achieving slightly better colour reductions on a bleachery effluent than a massive lime process, (i.e., respective removals of 95% and 88%). Their report also included cost comparisons and flow sheets for full scale systems including recovery. They estimate that alum treatment would be slightly cheaper. However, the method has apparently not been evaluated on a full scale basis as yet.

An interesting process for treatment of kraft bleachery effluent by precipitation and flocculation with iron salts is in full scale operation at the Kasugai mill of the Oji Paper Company, and has been investigated on a laboratory scale in Sweden (Freyschuss, 1974). In this process, effluent from the chlorination and extraction stages are treated. An iron solution is prepared by dissolving iron metal in the C-stage wastewater. This is combined with caustic extract and pH is adjusted with lime to 9 to 10. Colour reductions of 85% to 95% along with 70% to 80% KMnO₄ consumption, and 60% to 70% TOC and 15% to 25% BOD₇ removals are reported. Retention times of 1.5 to 2 hours and temperatures near 50°C are often needed to dissolve enough iron in the chlorination effluent, however, the concept is an interesting one and warrants further evaluation.

A recent report on a tour of the U.S.S.R., pollution abatement facilities (Anon, 1973) describes the treatment systems at Kotlas Pulp and Paper Mill on Lake Baikal. Kristyakov (1972) has also discussed

this treatment system. The mill manufactures a wide range of products including sulphite, kraft and NSSC pulps. After biological treatment, the secondary clarifier effluent is mixed with alum and then a polyacrylamide flocculant for colour removal. Subsequent to the chemical addition, the effluent is settled and polished by a system of filters before ultimate discharge to Lake Baikal. Average colour reductions from 1000 units down to 100 units are reported. No satisfactory solution to chemical sludge dewatering and disposal has yet been found; however, a 'semi-automatic' filter press system is being evaluated. Another recent Russian report by Luk'Yanova et al (1973) mentions the use of aluminum and ferric salts in amounts of 2% to 3% of waste mass to enhance the removal of lignosulphonates with lime and magnesia.

Beckhaus (1969) has evaluated a commercial flocculation agent Ferri-Floc (Al, Fe and Ti salts) for colour removal from a high-grade paper mill effluent and found that it gave better removals with easier sludge handling than the use of alum alone.

Willard and Scott (1972) compared ferric chloride and alum for colour removal from a secondary treated total kraft effluent and found both chemicals to be equally effective and capable of 85% removal efficiencies. They suggested that continuous monitoring of zeta potential would be necessary in order to control and optimize the coagulation process. This is because optimum colour removal is obtained in a very narrow pH band depending on the chemical used. Several studies have determined optimum pH and coagulant dosages, i.e., Tejera and Davis (1970) and more recently Olthof and Eckenfelder (1974). The latter authors found that the best pH for ferric sulphate varied between 3.5 to 5.5 and ranges for alum were slightly higher. These values will depend on waste characteristics and coagulant used, but similar results have been obtained by others. Chemical dosage required depends to a great extent on effluent colour as can be expected. In this study 250 to 500 mg/l Fe^{3+} or 250 to 400 mg/l Al^{3+} or 1000 to 1500 mg/l Ca^{2+} gave 85% to 95% colour removal (or 120 to 200 Pt-Co units residual). Lime or ferric sulphate were economically preferable to alum for all wastes tested.

The use of various combinations of chemicals and poly-electrolytes has been the subject of several investigations (usually laboratory scale) e.g., Kohn Cornejo (1973) treated board mill effluent with 170 mg/l alum, 1.1 mg/l of non-ionic polyelectrolyte and 16.5 mg/l activated silica. Willard and Scott (1972) found that organic polymers with either aluminum or iron salts improved colour removal processes. These authors also found that chemical sludge recycle increases the efficiency of alum up to 270%.

Generally speaking, careful selection of flocculant aids will improve coagulation, settling and colour removal efficiency. Day (1965) and others discuss the use of polymers in wastewater treatment in more detail and a list of commercial coagulation aids approved by EPA in the U.S., for water treatment is given by Anon (1971).

The main drawbacks to using either alum or iron salts are: (i) need for precise pH and zeta potential monitoring and control (this makes process automation difficult), and (ii) problems encountered in sludge handling. The sludges are notoriously difficult to dewater although improved equipment (filter presses and belt presses) are now available. Alum sludge disposal and regeneration are thoroughly discussed by Fulton (1969) and (1974) and Nielsen et al (1973). Alum recovery by H_2SO_4 following sludge incineration as proposed by Fuller (1973) and Bebin et al (1971) appears to be the method of choice at this time.

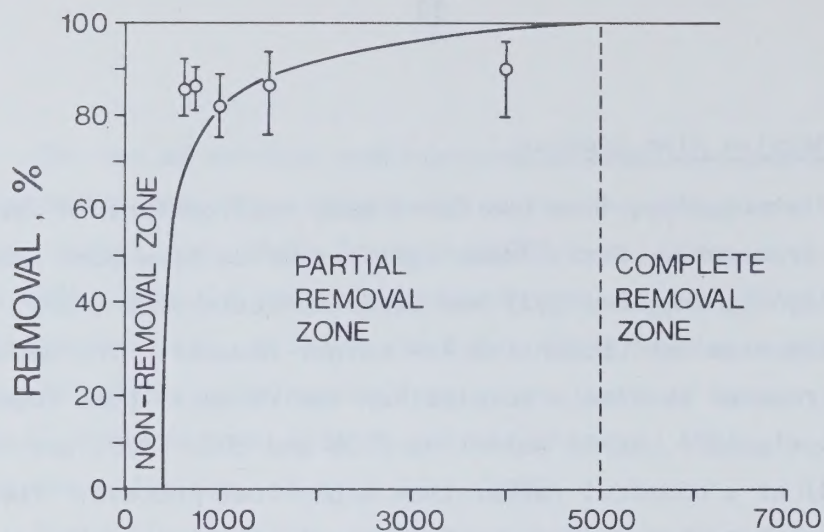
It can be seen from the brief selection of literature discussed here that aluminum and iron salts do provide good colour removal and are being used in a few full scale processes. The choice of chemical is largely dependent upon individual case economics as in water treatment or tertiary sewage treatment. However, in view of the process control and sludge problems encountered, it is unlikely that these chemicals will gain more than isolated use in the near future. A more likely choice of coagulant at this time would be lime (possibly with magnesium) as discussed next.

2.2.2 Massive lime process

Historically, lime has found many applications in water and wastewater treatment. Early investigations which have been summarized by Herbet (1962), Moggio (1952) and NCASI Bulletin #228 (1969) found that lime had excellent potential for colour removal. The mechanism for colour removal by lime precipitation has recently been identified (Bennett et al, 1971, NCASI Bulletins #239 and 242, 1970, and Swanson et al, 1973) as a chemical rather than a physical process. The main reactions are known to depend on the formation of insoluble calcium-organic salts. The molecular weight of the colour bodies also affects the degree of colour removal. In general, the high molecular weight materials tend to precipitate easily whereas the lower weights remain in solution. This type of behaviour is depicted in Figure 10.

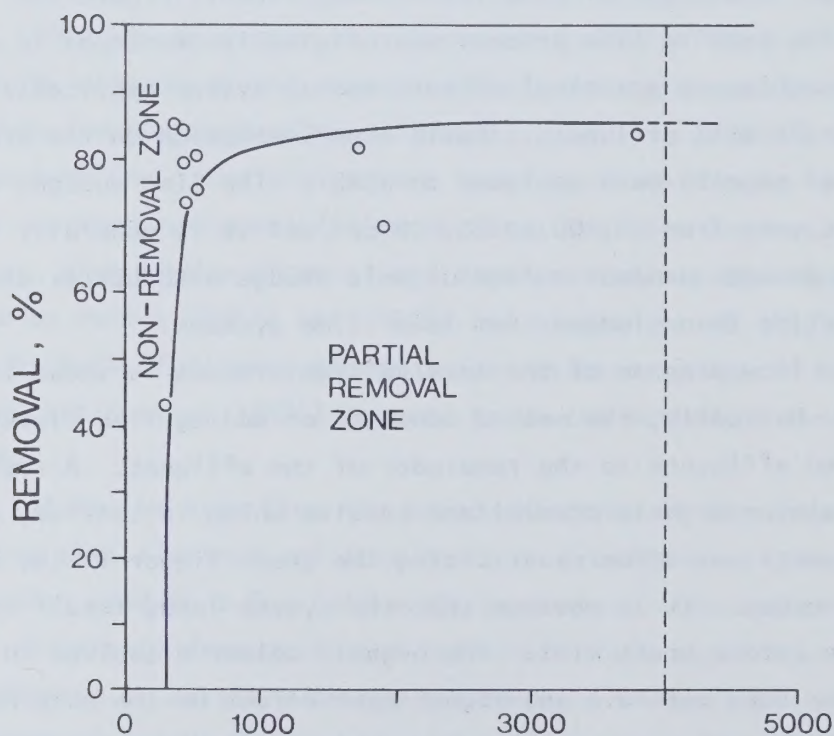
The massive lime process was originally developed in an attempt to achieve a practical colour removal system applicable to bleached kraft mill effluents. Basic experimentation on the process and eventual patents were assigned to NCASI. The lime dosages used in the process vary from 10,000 to 30,000 ppm and it is generally felt that these dosages produce a lime-organic sludge with better dewatering characteristics than sludges from lower lime systems.

A flow diagram of the massive lime process is shown in Figure 11. Basically, the method consists of adding lime slaked with the coloured effluents to the remainder of the effluent. A rapidly settling calcium-organic precipitate results which is settled, dewatered and subsequently used for causticizing the green liquor in the kraft recovery process. It is obvious that the system lends itself to integration into a kraft mill. The organic colour dissolved in the white liquor does not have any significant effect on the pulping process. These coloured materials are eventually disposed of by burning in the black liquor recovery system. As noted in the EPA study at Riceboro (Anon, 1974) and by Oswalt and Land (1973) considerable calcium (200 to 700 mg/l) remains in the decolourized effluent. To recover this calcium a recarbonation system using lime kiln stack gas is employed as shown in Figure 11.



M_w , ACID-INSOLUBLE COLOUR BODIES

- (a) WEIGHT AVERAGE MOLECULAR WEIGHT (M_w) OF ACID-INSOLUBLE COLOUR BODIES VERSUS THE DEGREE OF REMOVAL BY LIME TREATMENT



M_w , ACID-SOLUBLE COLOUR BODIES

- (b) WEIGHT AVERAGE MOLECULAR WEIGHT (M_w) OF ACID-SOLUBLE COLOUR BODIES VERSUS THE DEGREE OF REMOVAL BY LIME TREATMENT

FIGURE 10. EFFECT OF MOLECULAR WEIGHT OF COLOUR BODIES ON REMOVAL WITH LIME (SWANSON et al, 1973)

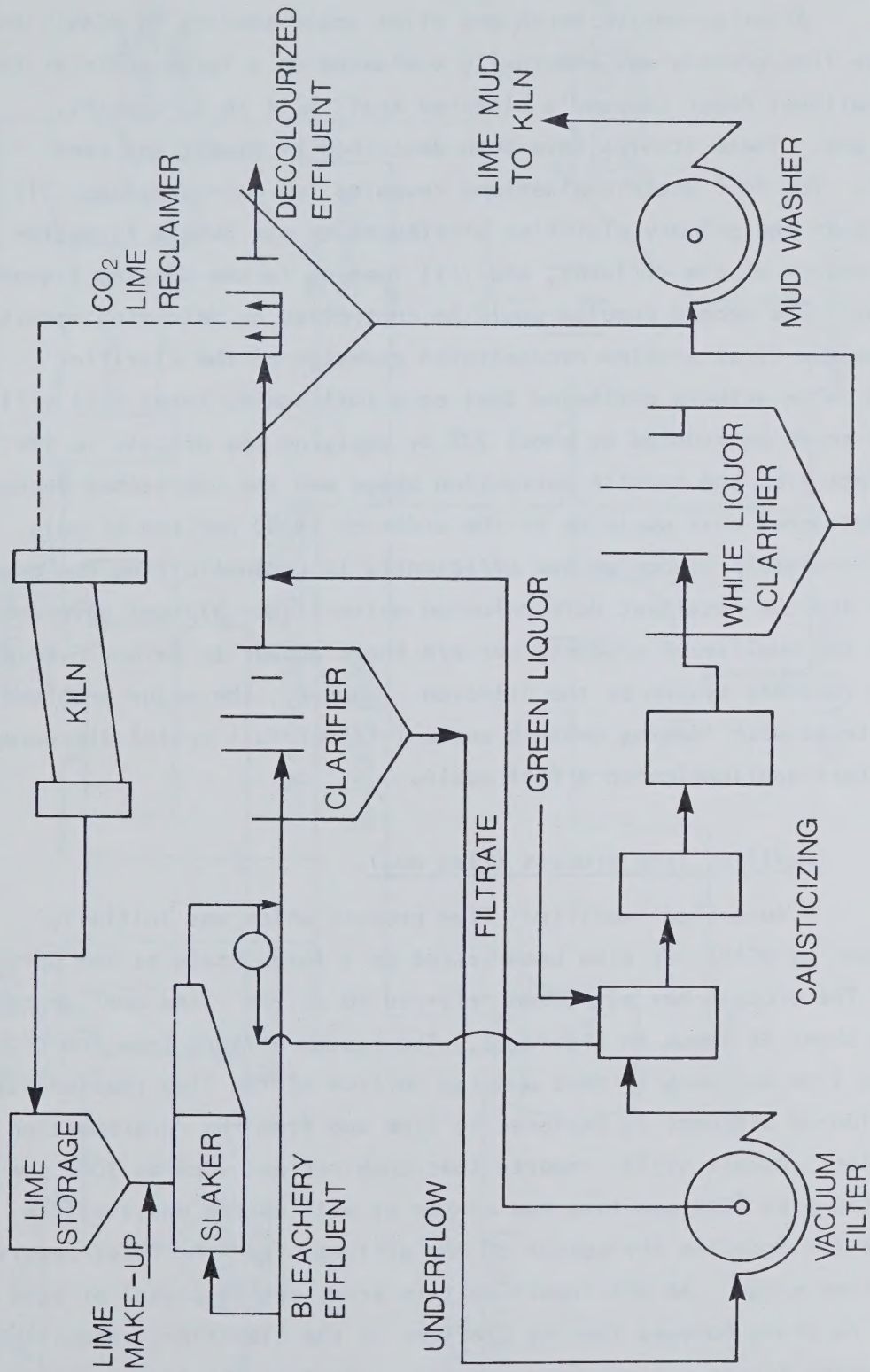


FIGURE 11. MASSIVE LIME PROCESS FOR COLOUR REMOVAL AT SPRINGHILL, LOUISIANA (GEHM, 1973)

After extensive bench and pilot scale testing by NCASI, the massive lime process was eventually evaluated on a large scale at the International Paper Company's bleached kraft mill in Springhill, Louisiana. These studies have been described by Oswalt and Land (1973). The full scale evaluations revealed two main problems: (i) foaming in the primary clarifier attributed to gas bubble formation upon contact of the effluent, and (ii) foaming in the cooking liquor systems. The second problem could be controlled by defoaming agents whereas the first problem necessitated redesign of the clarifier system. The authors estimated that on a full scale, total mill effluent colour could be reduced by about 72% by applying the process to the effluents from the caustic extraction stage and the unbleached decker. The additional cost would be in the order of \$1.80 per ton of pulp. The lime-organic sludge worked efficiently in recausticizing the green liquor and the resultant dark coloured white liquor did not adversely affect the quality of product, nor did there appear to be any overload on the recovery system by the dilution. However, the major problems encountered with foaming on this scale ($\approx 1/5$ of full scale) discourage its future application on a full scale.

2.2.3 Modified lime process (lime mud)

A so-called 'modified' lime process which was initially developed by NCASI has also been tested on a large scale at the Springhill mill. The process has also been referred to as the 'lime mud' process. A flow sheet is shown in Figure 12. The system differs from the massive lime approach in that a large portion of the lime reacted with the coloured effluent is replaced by lime mud from the recarbonation clarifier. Oswalt (1974) reports that combinations such as 3000 ppm fresh CaO plus 8000 ppm lime mud worked as well as the massive lime process for reducing the colour of the effluent from the first caustic extraction stage. An EPA report on this study is 'in press' at this time. At these dosages foaming problems in the clarifier, recausticizing and cooking liquor systems were reduced. Based on the two studies at Springhill, Oswalt (1974) concluded that the modified lime process is easier to control than the massive lime process and more adaptable to

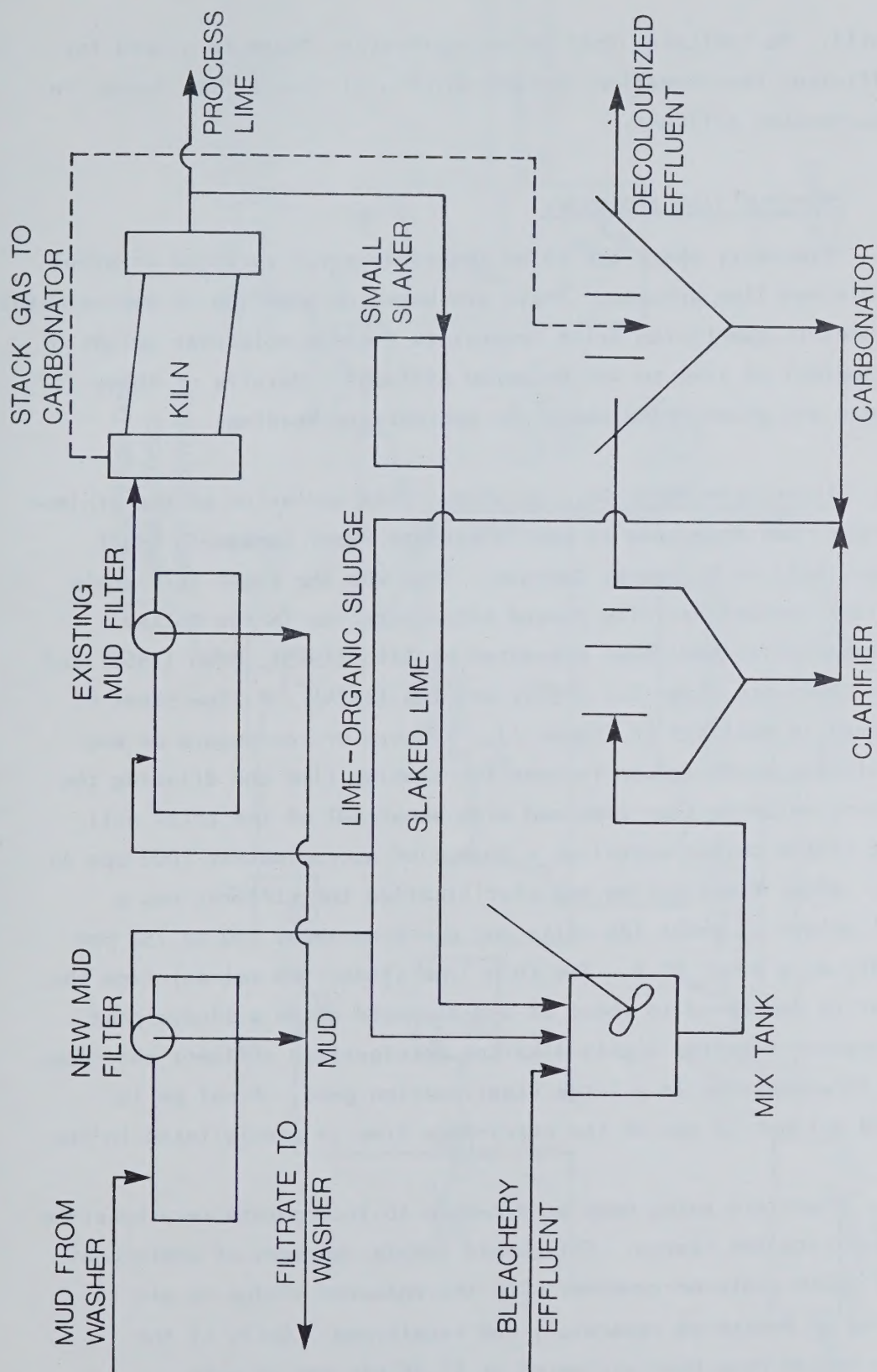


FIGURE 12. MODIFIED LIME OR LIME MUD PROCESS FOR COLOUR REMOVAL AT SPRINGHILL, LOUISIANA (GEHM, 1973)

kraft mill. He indicated that in both processes there is a need for more efficient recarbonation systems which will reduce lime losses in the recarbonated effluent.

2.2.4 Minimum lime processes

Presently there are three (possibly more) patented versions of the minimum lime process. These are based on addition of approximately stoichiometric quantities (with respect to average molecular weight of colour bodies) of lime to the coloured effluent. Details of these variations are given below under the appropriate headings.

2.2.4.1 Interstate Paper Co., version. This variation of the minimum lime process was developed at the Interstate Paper Company's kraft linerboard mill in Riceboro, Georgia. This was the first full scale lime colour removal facility placed into operation in the United States and results have been presented by Olin (1969), Anon (1968) and (1974), Interstate Paper Co. (1971) and EPA (1974). A flow sheet of the process is depicted in Figure 13. Evaporator condensate or any other suitable waste stream is used for slaking lime and diluting the lime slurry which is then combined with about 50% of the total mill effluent (≈ 1200 colour units) at a dosage of approximately 1000 ppm as Ca(OH)_2 . After flocculation and clarification the effluent has a residual colour of about 125 units and contains about 700 to 750 ppm of Ca(OH)_2 at a pH of 12.2. The thin lime sludge (2% solids) from the clarifier is dewatered to about 6% and disposed of in a sludge pond. At the present time the highly alkaline decolourized effluent undergoes natural recarbonation in a large stabilization pond. Final pH is ≈ 10.2 and all but 35 ppm of the carry-over lime is precipitated in the pond.

Plans are being made at Riceboro to incorporate recarbonation facilities into the system. This would enable recovery of additional lime mud which could be combined with the coloured sludge to aid in dewatering or dewatered separately and recalcined. Costs of the Riceboro system have been estimated at \$1.95 per ton of pulp.

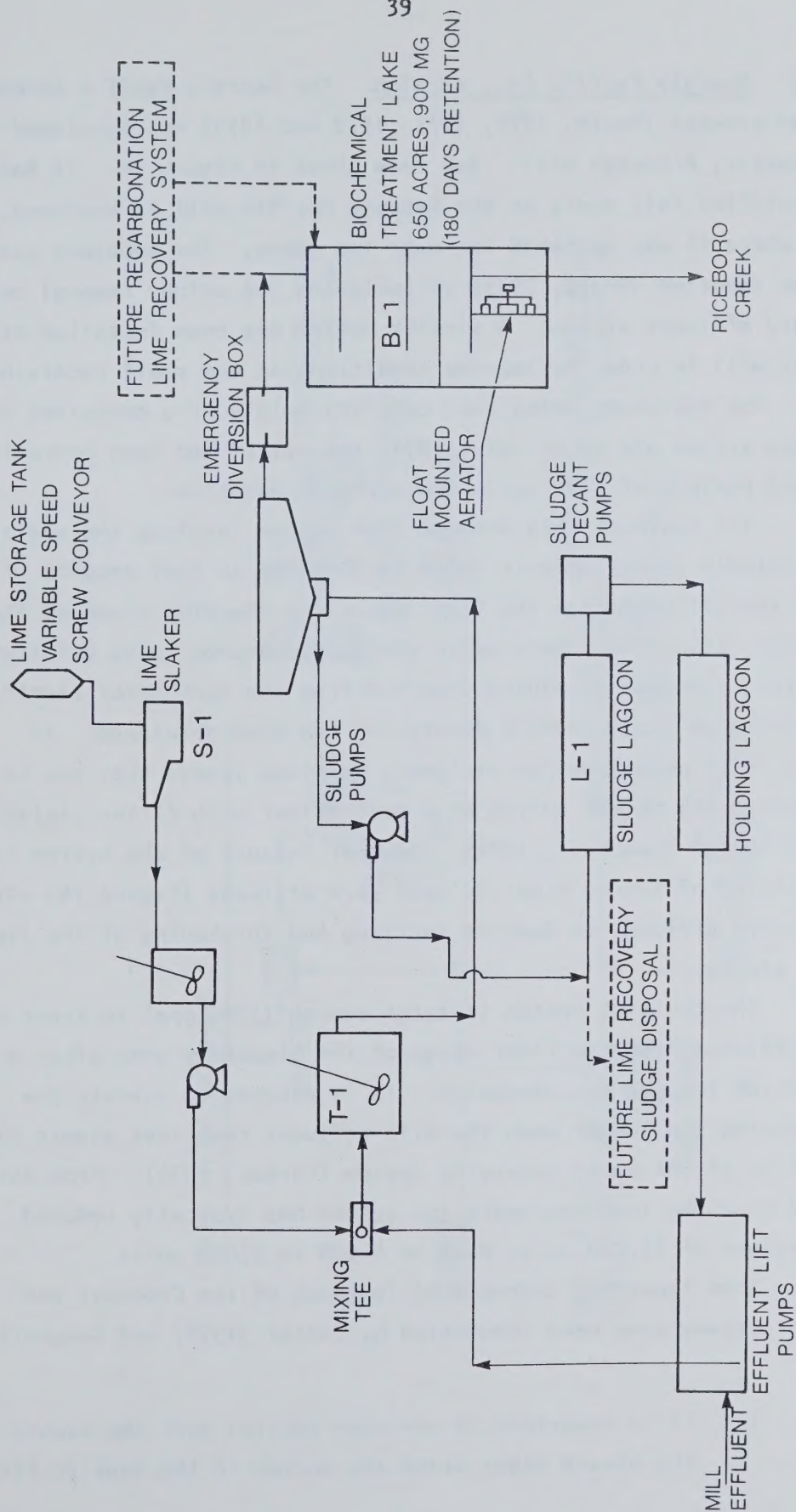


FIGURE 13. INTERSTATE PAPER CO., MINIMUM LIME PROCESS AT RICEBORO, GEORGIA
(EPA, 1974)

2.2.4.2 Georgia Pacific Co., version. The Georgia Pacific Company's patented process (Gould, 1970, 1971, 1972 and 1973) was developed at the Crossett, Arkansas mill. See flow sheet in Figure 14. It has been installed full scale at the Georgia Pacific mill in Woodland, Maine, where it was operated for over two years. The Woodland system has been reported (Gould, 1973) as achieving 90% colour removal on a bleachery effluent stream. A similar system has been installed at the Crossett mill in order to improve conditions in the small receiving stream. The equipment being used consists mainly of a converted water softening system and as of July, 1974, the system had been operational for short periods of time up to two weeks in duration.

The basis of this minimum lime method involves the addition of approximate stoichiometric (2000 to 3000 ppm as CaO) amounts of lime to the effluent from the first caustic extraction stage of the bleachery. Since the lime-organic sludge has proven to be difficult to dewater, a method of adding lime mud from the carbonator clarifier to the coloured sludge before dewatering has been developed. At Crossett, this procedure has yielded a combined sludge that can be dewatered to 50% to 60% solids on a belt filter with filter yields of 60 to 70 lb/ft² (Campbell, 1974). Another feature of the system is the combining of fibres from the wood yard effluent (Figure 14) with the coloured effluent to improve settling and thickening of the lime-organic sludge.

The Crossett system is large enough (3000 gpm) to treat the entire effluent from the first stage of the bleachery even after a proposed 700 ton per day expansion. It is planned to operate the system during the summer when the mill effluent comprises almost the entire flow of the small receiving system (Carter, 1974). From data obtained over the last two years the system has typically reduced colour values of 12,000 units down to 4,000 to 5,000 units.

Some important operational features of the Crossett and Woodland systems have been identified by Carter (1974) and Campbell (1974):

- (i) it is important to exercise control over the caustic in the bleach plant since the sodium in the caustic filtrate

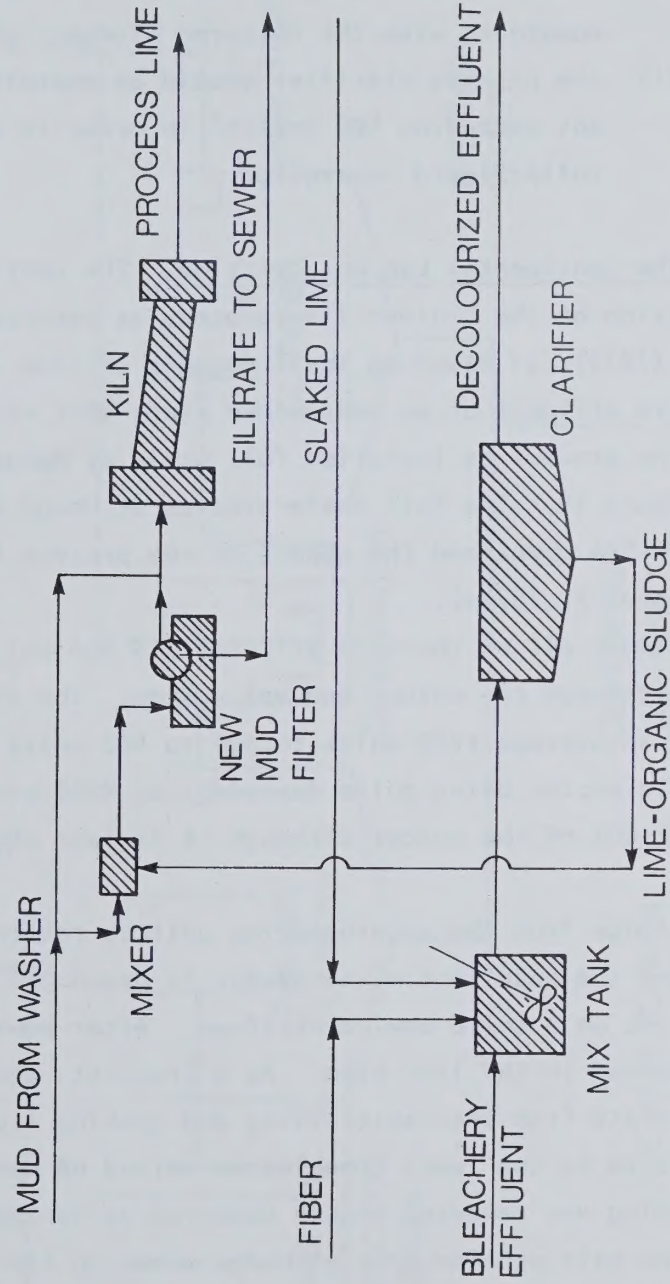


FIGURE 14. GEORGIA PACIFIC CO., MINIMUM LIME PROCESS
(GOULD, 1973)

appears to interfere with settling and compete with the lime-organic reaction;

- (ii) for the same reason as (i) it is essential that the lime mud be thoroughly washed of residual sodium before combining with the coloured sludge; and,
- (iii) the primary clarifier should be operated at a rise rate not exceeding 400 gpd/ft^2 in order to achieve good solid-liquid separation.

2.2.4.3 The Continental Can Co., version. The Continental Can Company version of the minimum lime process as reported by Spruill (1971) and (1973), is based on small dosages of lime ($\approx 1000 \text{ ppm CaO}$) to the entire effluent of an unbleached kraft-NSSC mill. The flow sheet for the process as installed full scale at Hodge, Louisiana, is shown in Figure 15. The full scale studies at Hodge were partially funded by an EPA grant and the report on the project has been published recently (Spruill, 1974a).

Almost all of the mill effluent (13 mgd out of a total 15 mgd) passes through the colour removal system. The system reduces colour from an average 1200 units to 300 to 400 units with individual removal efficiencies being quite dependent on NSSC production which accounts for 60% of the colour although it is less than 25% of total production.

Sludge from the recarbonation unit is returned to the primary clarifier and the resultant mixed sludge is drawn off for dewatering to $\approx 35\%$ solids on a solid bowl centrifuge. After dewatering, the sludge is burned in the lime kiln. As a Crossett, the colour sludge is kept separate from the causticizing and cooking liquor systems. This appears to be the least troublesome method of operation since no serious foaming was reported as had occurred at Springhill.

The main problem area at Hodge seems to lie in the recarbonation part of the system. Colour removal in the primary clarifier is usually about 85%, however, during recarbonation, colour increases and about 35% to 40% of the initial colour remains after secondary clarification. Various operational procedures are being investigated

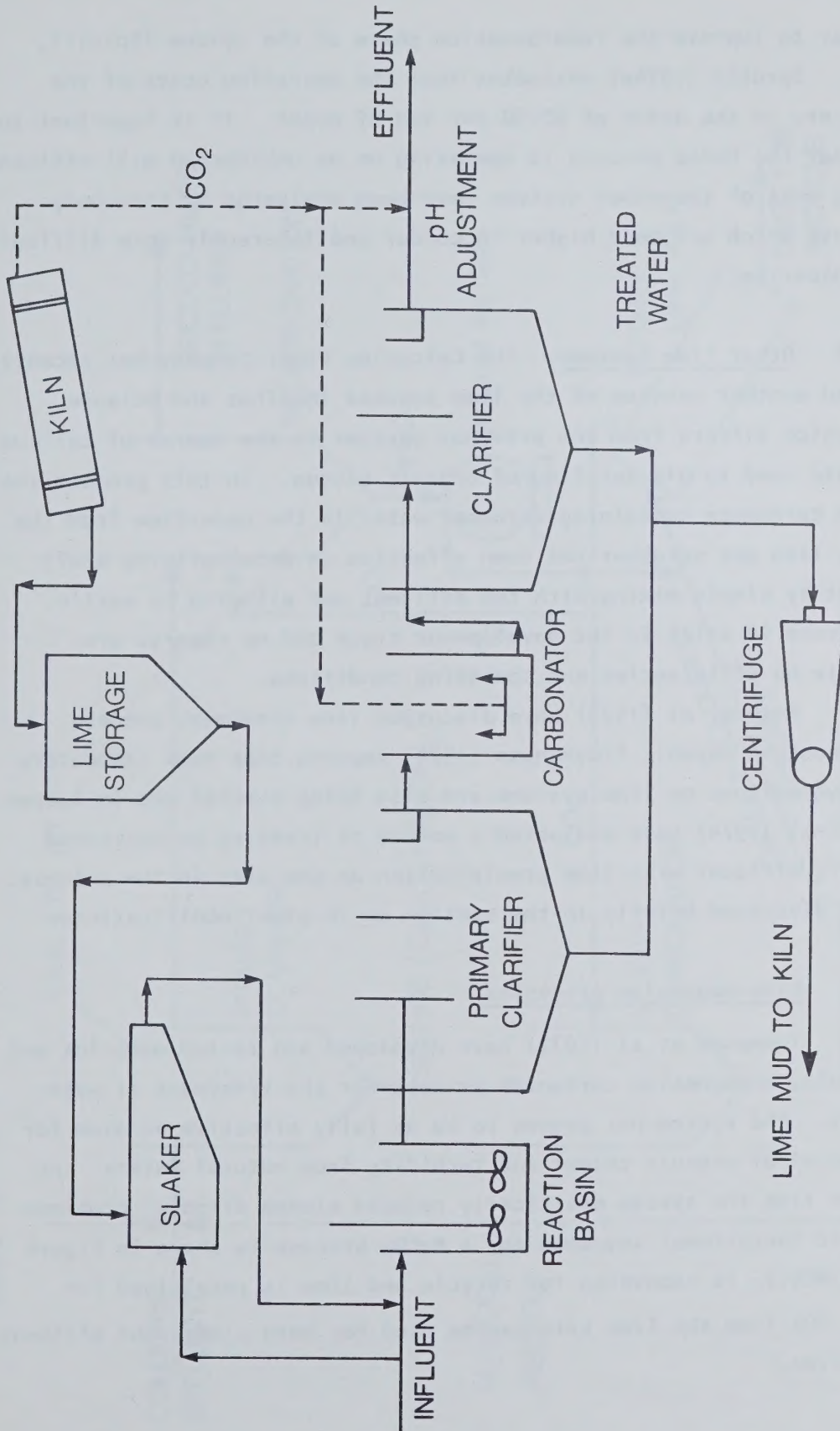


FIGURE 15. CONTINENTAL CAN CO. INC., MINIMUM LIME PROCESS AT
HODGE, LOUISIANA (GEHM, 1973)

in order to improve the recarbonation phase of the system (Spruill, 1974b). Spruill (1974a) estimates that the operating costs of the system are in the order of \$0.50 per ton of paper. It is important to note that the Hodge process is operating on an unbleached mill effluent whereas most of the other systems have been evaluated on bleachery effluents which are much higher in colour and inherently more difficult to decolourize.

2.2.4.4 Other lime systems. The Calcasieu Paper Company has recently patented another version of the lime process (Mailhos and Delaune, 1972) which differs from the previous systems by the source of calcium carbonate used to aid settling of organic sludge. In this process the calcium carbonate containing scrubber water in the underflow from the primary lime gas scrubber has been effective in decolourizing kraft effluent by simply mixing with the effluent and allowing to settle. The process is still in the development stage and no reports are available on efficiencies and operating conditions.

Kato et al (1973) have discussed lime treatment process development in Japan. Freyschuss (1974) reports that some laboratory scale evaluations on lime systems are also being carried out in Sweden. Nayak et al (1974) have evaluated a method of treating concentrated bleachery effluent with lime precipitation as one step in the process. This is discussed briefly in the section on in-plant modifications.

2.2.5 Lime-magnesium processes

Thompson et al (1972) have developed and tested on pilot and full scale, a magnesium carbonate process for the treatment of water supplies. The system has proven to be as fully effective as alum for the removal of organic colour and turbidity from natural waters. At the same time the system drastically reduces sludge disposal problems. The basic operational sequence for a $MgCO_3$ process is shown in Figure 16. $Mg(HCO_3)_2$ is recovered for recycle and lime is recalcined for reuse. CO_2 from the lime kiln can be used for both sludge and effluent carbonation.

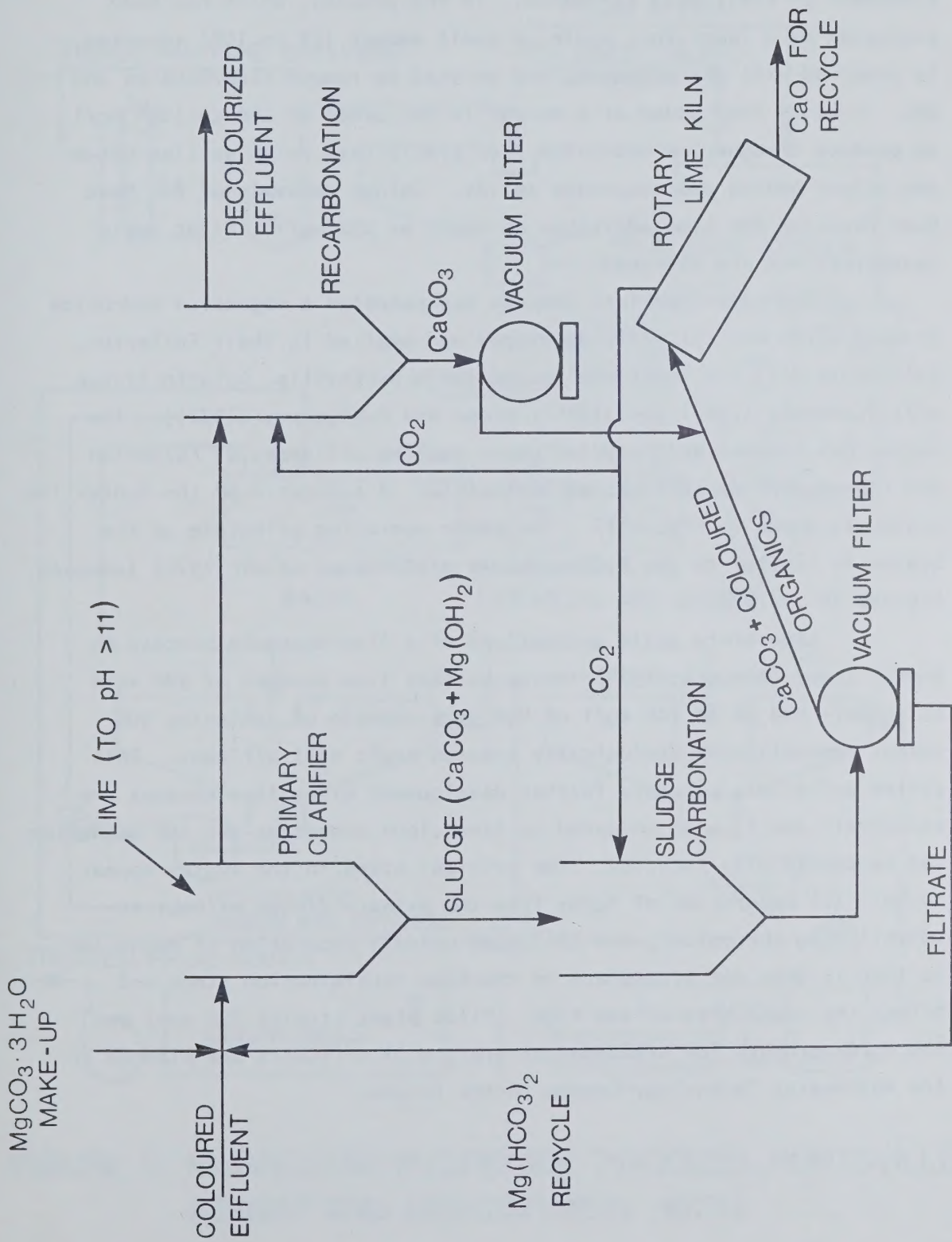


FIGURE 16. MAGNESIUM CARBONATE PROCESS DIAGRAM

Rapson et al (1973) describe a seawater-lime process which has been developed at the Nova Scotia Research Foundation for the treatment of kraft mill effluents. In the process, which has been evaluated on a laboratory scale, a small amount (5% to 10%) seawater is combined with the effluent, and aerated to remove bicarbonates and CO_2 . Lime is then added at a dosage in the order of 250 to 1000 mg/l to produce a magnesium hydroxide rich precipitate which settles out the colour bodies and suspended solids. Colour removals of 80% have been reported for lime additions as small as 250 mg/l. Pilot scale investigations are planned.

The Kimberly-Clark Company has patented a magnesium hydroxide process which was initially developed and applied in their Fullerton, California mill and later applied in their Huntsville, Ontario tissue mill [Lecompte (1967) and (1966), Gropp and Montgomery (1972)]. The system has treated and recycled paper machine effluents at Fullerton and tissue machine effluent at Huntsville. A schematic of the Huntsville system is shown in Figure 17. The basic operating principle of the system is similar to the MgCO_3 process of Thompson et al (1972) (compare Figures 16 and 17).

Laboratory scale evaluations of a lime-magnesia process by Domtar Ltd., (Vincent, 1974) indicates that lime dosages of 500 mg/l as Ca(OH)_2 and 50 to 100 mg/l of MgO were capable of achieving 90% colour removals on a biologically treated kraft mill effluent. This system definitely warrants further development since lime dosages are relatively small, when compared to lime-alone processes and the magnesium can be continually recycled. The critical steps in the system appear to be: (i) separation of MgCO_3 from the primary sludge without re-solubilizing the colour, and (ii) good overall separation of magnesium so that it does not accumulate in the lime recalcination steps and affect the reactivity of the lime. Pilot plant studies (20 gpm) on the MgCO_3 process for treatment of kraft mill effluents are planned at the Wastewater Technology Centre in the future.

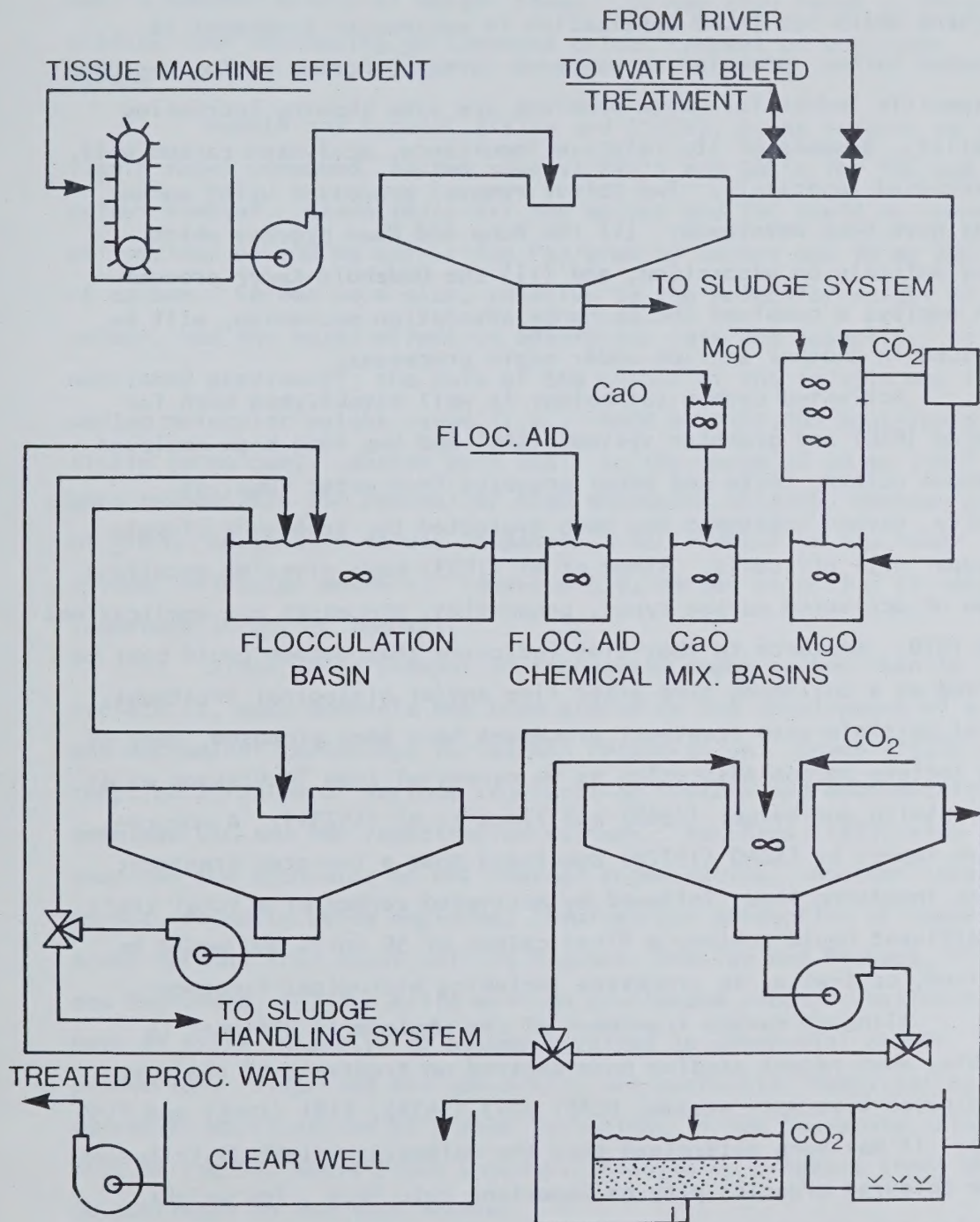


FIGURE 17. MAGNESIUM HYDROXIDE PROCESS HUNTSVILLE
(GROPP AND MONTGOMERY, 1973)

2.3 Carbon Adsorption

Many materials exhibit adsorption properties, but the main adsorbent which has found application in wastewater treatment is activated carbon (granular or powdered forms). Porous resins designed for specific industrial waste problems are also showing increasing potential. Because of its relative importance, activated carbon will be discussed separately. Two colour removal processes using porous resins have been developed: (i) the Rohm and Haas process which relies entirely on adsorption, and (ii) the Uddeholm-Kamyr process which employs a combined ion exchange adsorption mechanism, will be discussed in another section under resin processes.

Activated carbon technology is well established both for powdered (PAC) and granular systems (GAC) and has long been employed to remove colour, taste and odour organics from water supplies. Recently, carbon treatment has been evaluated for treatment of pulp and paper mill effluents. Timpe et al (1973) have given an excellent review of activated carbon types, properties, processes and applications up to 1970. Research to that time indicated that carbon could best be utilized as a polishing step after lime and/or biological treatment. Several multiple-step treatment processes have been proposed, many of which include carbon adsorption as an essential step [McGlasson et al (1966), Smith and Berger (1968) and Timpe et al (1973)]. A comprehensive report by EKONO (1972a) concluded that a two-step treatment process involving lime, followed by activated carbon of a total kraft mill effluent could achieve a final colour of 50 units and would be preferred, cost-wise, to processes including biological treatment.

Although carbon treatment of the whole mill effluent is possible, most recent studies have centred on treatment of the more concentrated bleachery stream, NCASI #273 (1974), #181 (1965) and #199 (1967). It has been determined that the molecular weight distribution of the coloured organics play an important role (e.g., low weight molecules are adsorbed more readily than higher weights). Since the larger weight molecules are removed in lime treatment, it would seem that carbon would best be employed after lime treatment to remove low molecular weight species. In this regard, refer to the molecular

weight distribution after lime treatment in Figure 10. In addition, carbon with large pore sizes would be better for adsorbing molecules over a broader molecular weight range. It was also found in these studies that decreasing pH favoured colour removal on activated carbon.

Rankin and Benedek (1973a and 1973b), using Indulin as a lignin model compound, tested several PAC's and GAC's for TOC and colour removal. Essentially all the colour and TOC could be removed at loadings of 100 mg colour (as Pt)/gram of carbon and 10 mg TOC/gram of carbon. Carbon pore size, relative to the molecular weight of the colour, had the major effect on adsorption rate and capacity. As mentioned previously, the bulk of the colour of the Indulin was in the medium molecular weight range (i.e., <4000 or >150,000 contribute little to colour). Carbon pore radii in the range of 20 to 150 Å were responsible for removal of high molecular weights, whereas pores of ≤ 10 Å radius were mainly responsible for removal of the lower (<4000) molecular weights. Consequently, carbon selection is very important in colour removal.

Since it is cheaper to regenerate spent carbon than to replace it, much emphasis has been placed on the development of a safe and economical technology for carbon regeneration. Loven (1973) has compiled a review of various regeneration systems and economically examined GAC and PAC reactivation systems. Hutchins (1973) also has examined the economics of GAC thermal regeneration. Another interesting aspect, recently being explored, involves the production of commercial grade carbons from spent pulping liquors (Barclay and Prahacs, 1971, and MacDonald, 1973). Mills with an overloaded recovery system may have an extra incentive to become involved in commercial carbon production. Timpe and his co-workers are currently investigating potential applications of carbon technology in the Pensacola, Florida mill of the St. Regis Paper Company. Reports on progress there should be published in the near future.

It is apparent that, as had been demonstrated in the municipal and other industrial waste areas, activated carbon has great potential as part of a two or multiple-step treatment process for pulp and paper

mill effluent treatment. Its role should become more important as more emphasis is placed on water reuse within the mill. The results of various investigations show that the quality of the carbon treated effluents can be sufficiently high to allow internal recycle.

2.4 Ozonation

Ozone has long been utilized for disinfection of water supplies and more recently it has been employed successfully in municipal and industrial wastewater treatment applications. Most organic compounds in wastewater, for example, phenols, benzene and its derivatives, tertiary amines, chlorinated hydrocarbons, sulphides, etc., can be oxidized by ozone. Reviews of ozonation technology have been compiled by Evans (1972), Diaper (1972) and Majumdar and Sproul (1974).

As the coloured material in pulp and paper mills are resistant to conventional biological oxidation, it is only natural that the more rigorous oxidation provided by ozonation would eventually be investigated for decolourizing. In general, ozonation, similar to other strong oxidants, alters or breaks down the chemical structure of the colour forming materials so that their light absorption spectrum is shifted away from the visible wave lengths. Ozone demand is largely dependent upon the initial BOD or COD of the wastewater, therefore, ozonation is best used as a polishing step subsequent to biological treatment.

Laboratory scale evaluations of ozone for decolourization of selected pulp and paper mill effluents have been carried out by Nebel et al (1974a and 1974b) and NCASI #269 (1974). In the former study, daily ozone requirements to treat four different mill effluents were estimated as shown in Table 4.

A typical result after ozonation of an effluent from a bleach board mill is shown in Figure 18. Note the colour reversion phenomenon, i.e., a slight increase in effluent colour with time after initial ozonation. This reversion was also observed in the NCASI #269 (1974) and Bauman and Lutz (1974) studies and is generally limited to a colour increase of less than 10%.

TABLE 4. DAILY OZONE REQUIREMENTS TO TREAT MILL EFFLUENTS
(NEBEL ET AL, 1974a and 1974b)

Mill	Type	Initial Colour APHA Units	Req'd Colour APHA	O ₃ Req'd (ppm)	Effluent Flow (mgd)	Daily O ₃ Req'd (lb)	Daily ¹ Op. Cost (\$)	Capital ² Cost (\$x1000)
A	Kraft integrated mill	520	100	70	15	8750	394	315
B	Kraft integrated mill	900	200	81	16	10800	486	372
C	Kraft & NSSC bleached board mill	1600	200	143	25	29780	1340	975
D	Paper mill paperboard from reclaimed paper	170	50	29	25	605	48	95

¹ Operating Cost for Ozone alone.

² Capital Cost for Ozone Generators alone.

There is a tendency for ozonation to increase the BOD of the decolourized effluent, particularly at higher O₃ dosages, and is probably due to the conversion of the colour molecules into a structure more susceptible to biological oxidation. This behaviour has been noted by Nebel et al (1974a and 1974b) and NCASI (1974). An example of this is depicted in Figure 19.

In the NCASI (1974) studies, twelve different classes of mill effluent, including total mill effluents, bleachery effluents, and lime decolourized effluents were ozonated in a small laboratory ozonator. The ozone requirements for selected effluents are summarized in Table 5.

In general, the NCASI study concluded that 15 to 50 colour units were removed per mg of ozone for bleachery effluents, only 4 to 5 units/mg O₃ in total kraft mill effluents and less than 1 unit/mg O₃ in lime decolourized effluents.

Few pilot or full scale evaluations of ozonation as a decolourization process have been carried out. However, pilot scale results at the P.H. Glatfelter Company mill in Spring Grove, Pennsylvania, have been recently reported by Bauman and Lutz (1974). In this investigation, the biologically treated (contact stabilization activated sludge)

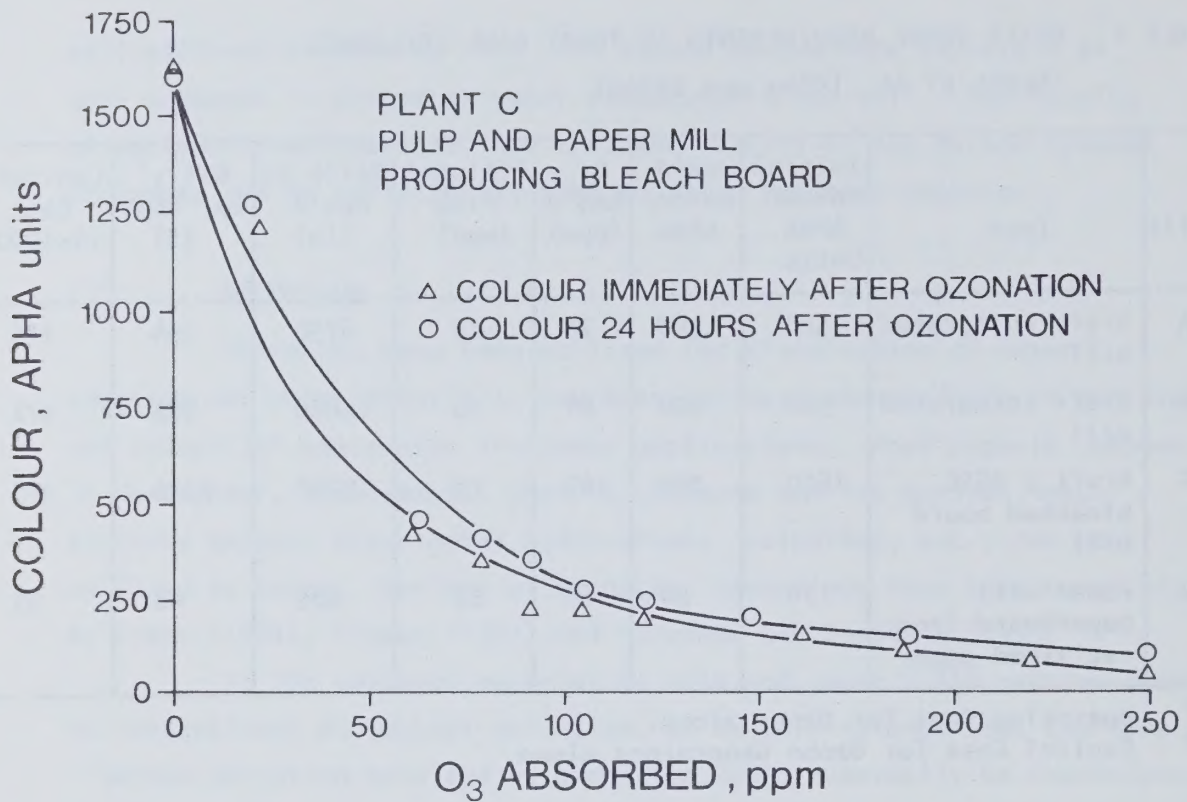


FIGURE 18. COLOUR REDUCTION BY OZONE (NEBEL et al, 1974 a & b)

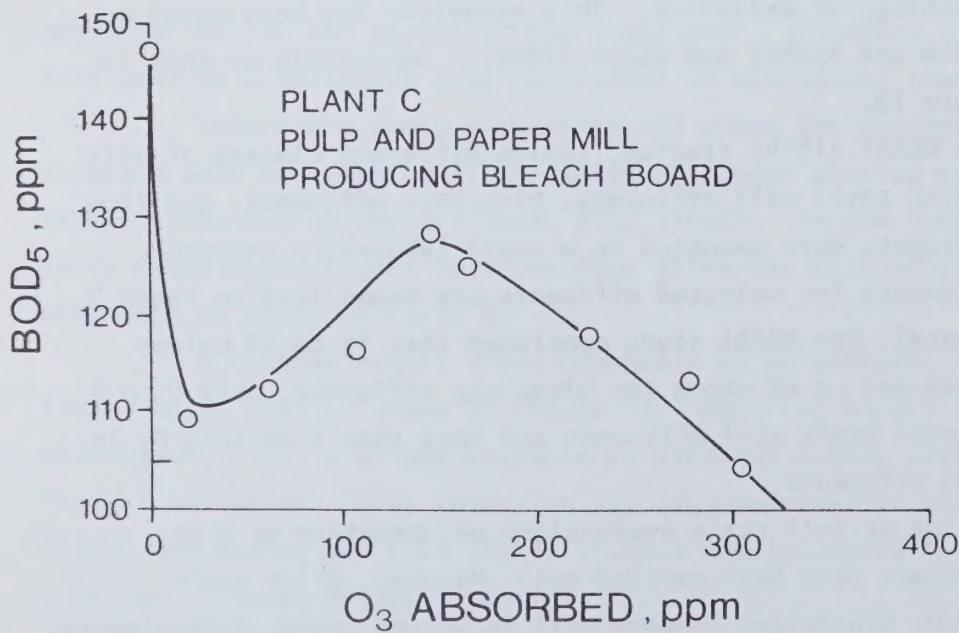


FIGURE 19. BOD₅ REDUCTION BY OZONE (NEBEL et al, 1974 a & b)

total mill effluent from a bleached kraft pulp and fine papers mill was treated in a 5 gpm pilot plant consisting of four series reactor towers. It was found that at an ozone dosage of 30 ppm (little improvement was found in going to higher dosages), the initial colour of the effluent of 400 to 900 units could be reduced to 150 to 200 units. Coliform reductions were in excess of 90% and average BOD increased from 10 to 20 mg/l. CaCO_3 scaling of the ozone spargers was reported. However, an increase in sparger pore size and HCl cleaning remedied these problems.

TABLE 5. OZONE REQUIREMENTS FOR DECOLOURIZATION OF SELECTED PULP AND PAPER MILL EFFLUENTS (NCASI, 1974)

Stream	Initial Colour (APHA)	Ozone Required for 75% Colour Reduction (mg/l)
Lime decolourized hardwood caustic bleach effluent extract	425	100
Kraft mill total secondary treated effluent	540	85
NSSC total mill effluent sodium base	7500	>850

Bauman and Lutz (1974) derived a regression equation from their laboratory data which expresses colour removal as a function of ozone dosage, COD, initial colour, suspended solids and units of colour lost.

$$\begin{aligned}
 \text{Colour Removal (\%)} = & 67.4 + 0.055 (\text{ppm O}_3) - 0.11 (\text{ppm COD}) \\
 & - 0.069 (\text{units of initial colour}) \\
 & + 0.16 (\text{ppm suspended solids}) \\
 & + 0.14 (\text{units of colour lost}) \quad \dots\dots(1)
 \end{aligned}$$

Excellent agreement between results predicted by Equation (1) and actual pilot plant data was reported. On the basis of information presently available, it certainly appears that further development work

[i.e., determining optimum contact times, best gas liquid transfer systems and influence of important process variables such as those indicated in Equation (1)] is required on decolourization processes using ozone.

It is very difficult to estimate operating costs for ozonation systems since the major component of ozonation costs is dependent upon the method of ozone generation. For example, Nebel et al (1974a and 1974b) report that the simplest and most economical method of generating ozone is a process whereby oxygen from a liquefaction plant is converted to ozone which in turn is applied to the ozone reactor. The moist O_2 from the reactor could then be utilized in other mill processes such as oxygen bleaching of pulp or pure oxygen activated sludge wastewater treatment systems. Few mills have the facilities for utilizing the moist O_2 ; consequently, the reactor O_2 off-gas must be recompressed, dried and returned to the ozone generator. This recycle process has a higher power requirement, thus a higher cost. Nebel et al (1974a and 1974b) estimate ozonation costs (operating plus amortized capital costs) for secondary treated total kraft mill effluents to be in the range of 2.8 to 6.4¢/1000 gallons treated. Capital and operating costs for four different effluents have been presented in Table 4. Bauman and Lutz (1974) calculated costs from their pilot scale studies of \$2.00 to \$2.75/ton of pulp. More pilot scale and initial full scale demonstration studies are recommended in order to determine not only the capacity of ozonation for colour, BOD and COD removal, but also to generate more reliable economic data.

2.5 Resin Separation and Ion Exchange Processes

As pointed out previously, some specially designed synthetic resins have shown a good ability to adsorb coloured organics from pulp and paper mill effluents. Rebhun and Kaufman (1967) found certain carbons and resins equally effective for removing colour from treated effluents. Sanks (1973) made an extensive study of ion exchange and concluded that properly selected resins perform as well as the best carbons with respect to colour removal from kraft bleachery effluents. Research by Ruzickova (1970), Lindberg (1973) and others on the use of

adsorption and ion exchange resins is encouraging, although, to be economical, it is desirable to regenerate the resin with other waste streams available in the mill.

Presently only two processes have evolved to the point of large scale demonstration and development. These are the Rohm-Haas process and the Uddeholm-Kamyr process. Both are discussed in further detail in the following section. For a detailed review on ion exchange processes, the reader should consult Lynch and Mintz (1972).

2.5.1 Rohm and Hass process

This adsorption process was developed out of extensive research carried out by the Rohm-Haas Company in the United States on specific resin treatment of pulp and paper mill effluents. The physical and chemical characteristics of the macroreticular resins used are described by Simpson (1972) and Rohm and Haas (1971). Colour removal and industrial waste treatment study results are given by Gulbrandson et al (1973), Kunin and Downing (1970), Rock et al (1974) and Rohm and Haas (1971).

The most recently applied resin has the trade name Amberlite XAD-8, a highly cross-linked hydrophilic, porous polymer containing no ion exchange groups. Therefore, the mechanism of colour removal is solely a sorption phenomenon. Results of recent field tests of the system have been described by Rock et al (1974). A schematic drawing of the system is shown in Figure 20. Using the system to treat a combined caustic extract-chlorination bleachery effluent resulted in colour removal of 70% to 95% and average BOD and COD removals of 33% and 43%, respectively. Prefiltration of the bleachery effluent was necessary in order to prevent fouling of the resin columns. White liquor was used for resin regeneration. For the 700 ton per day mill, it was calculated that capital investment for a full scale system would be \$1,495,000, with operating costs of \$0.70 per ton of paper. Evaporator capacity would also have to be increased by 1.3% to 5.0%. The fact that a low pH (≤ 2.5) is required for optimum efficiency and that a buildup of chlorides in the pulping process is possible, are two potential disadvantages of the system.

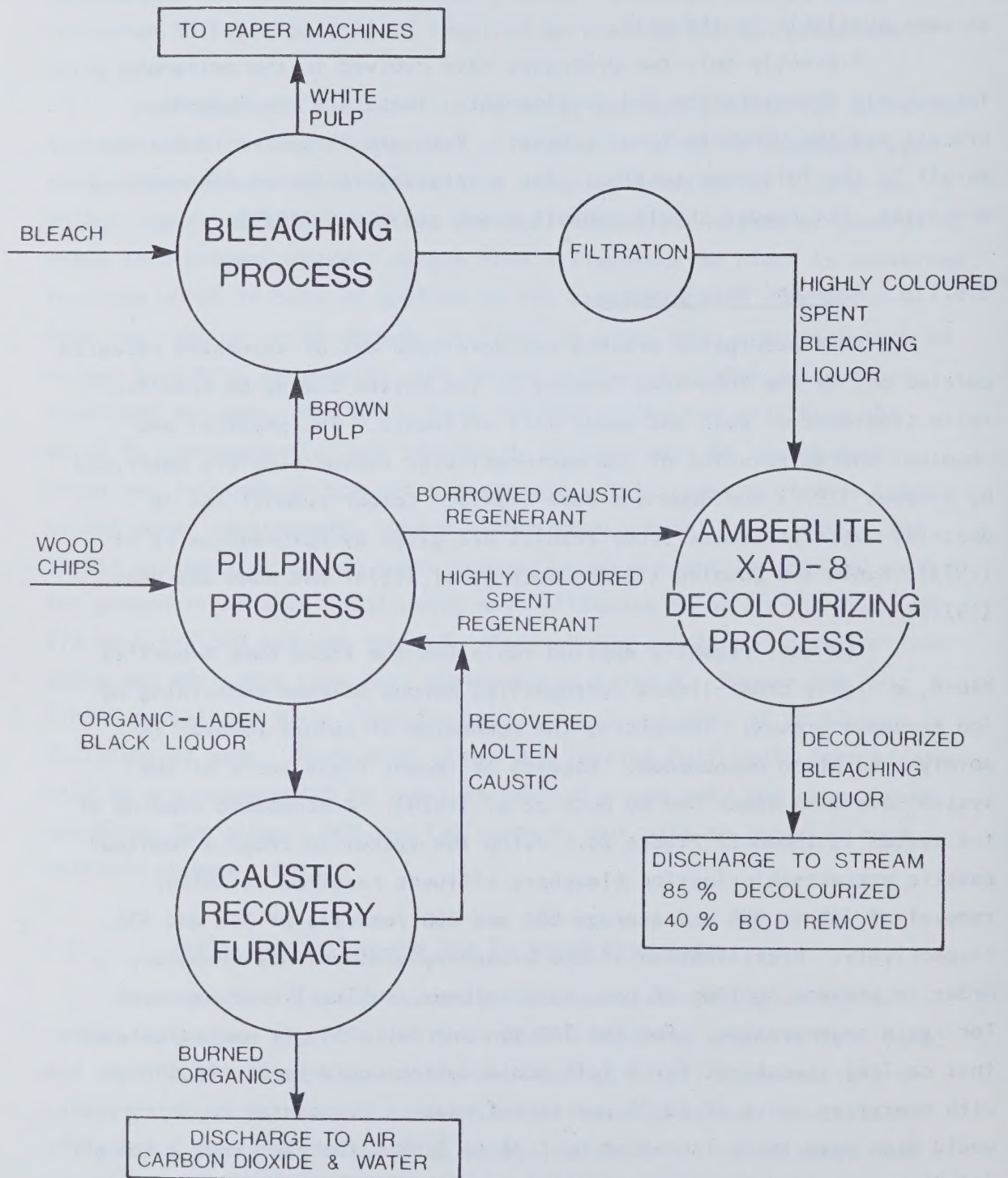


FIGURE 20. ROHM AND HAAS RESIN PROCESS (ROCK et al, 1974)

2.5.2 Uddeholm-Kamyr process

Although frequently referred to as the Swedish ion exchange process, the mechanism of the Uddeholm-Kamyr system appears to be a combination of ion exchange and adsorption. As with most other colour removal systems, emphasis is being placed on treatment of the first caustic extraction effluent of the bleachery. It has been claimed, however, that the process is applicable to any coloured waste stream and that colour removals of essentially 100% can be achieved on total mill effluents.

No description of the chemical and physical properties of the resin employed could be found, but apparently the resin is of a weak anionic type which can be regenerated in two steps [i.e., caustic (1 to 2 N) and acid reactivation with H_2SO_3 or spent H_2SO_4]. The organic coloured material in the regenerant stream can be burned off in the recovery furnace [Lindberg (1973) and Anderson et al (1973)].

Currently, treatment of a kraft bleachery effluent (first caustic extraction stage) by the Uddeholm process is being carried out at the 300-ton per day Skoghall mill of the Uddeholm Company of Sweden. A flow sheet of the process is shown in Figure 21. Detailed results are provided in a paper by Lindberg (1973). The initial caustic extraction effluent has a colour of 14,000 ppm, BOD of 800 ppm and a COD of 2400 ppm. At through-puts of up to 18 bed volumes average colour reductions were 80% to 90%, with concurrent BOD and COD reductions of 50% and 80%, respectively. Pilot scale work on the same process has been carried out at the Swedish Cellulose Company also (Freyschuss, 1974). In addition, Kamyr Inc., in the United States is presently using a 20 gpm mobile plant to collect operational data on the system at several North American mills (Morris, 1974). A full scale system is also in operation in Japan at the Daishowa Paper Company at Iwanuma. Here, the system is reported to achieve 90% to 95% colour removal on a caustic extraction effluent. Operating costs of the system have been estimated, based on Swedish experience, at \$0.90/ton of pulp. Potential drawbacks for the systems are the same as the Rohm and Haas process and include chloride buildup and requirement for a 2% to 3% increase in evaporator capacity.

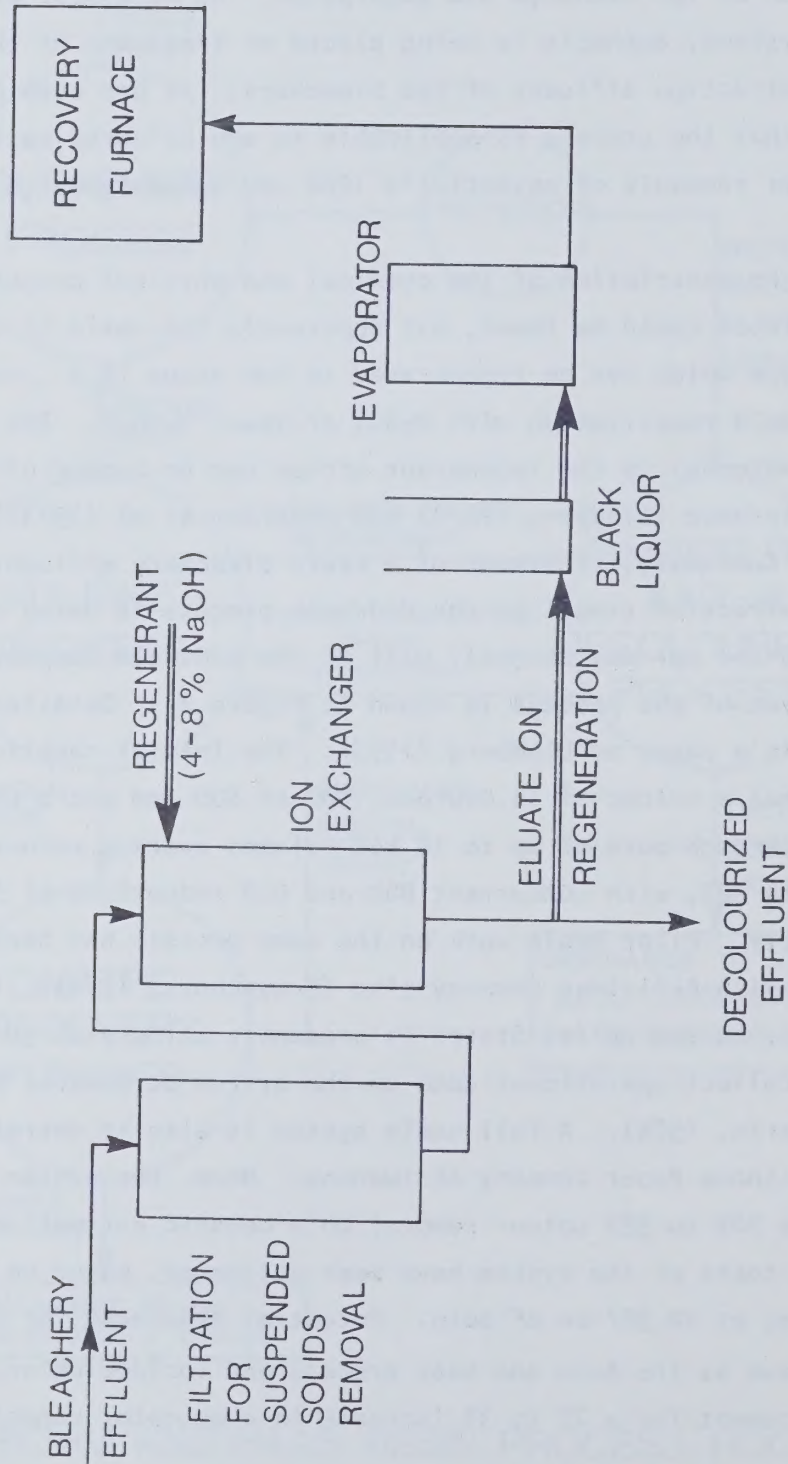


FIGURE 21. UDDEHOLM - KAMYR RESIN PROCESS (LINDBERG, 1973)

2.6 Adsorptive Bubble Separation Processes (ABSP)

Adsorptive bubble separation processes include microflotation, precipitate flotation, ion flotation and other processes. Terminology and nomenclature has been delineated by Karger et al (1967), while basic concepts of adsorptive bubble separation methods have been discussed by Lemlich (1968) and (1972) and others. Wastewater treatment applications have been described in numerous papers (e.g., Grieves, 1965 and 1970, Grieves and Bewley, 1973, Cassell et al, 1968, Herschmiller, 1972 and Wood, 1974).

The natural foaming tendencies of pulp and paper wastewaters were examined sometime ago by Waldichuk (1964) who concluded that mixing of the acid and caustic streams of the bleachery produces the main foaming problem. This foaming potential naturally led to an interest in foam fractionation which relies on the natural surface activity of lignin, causing the lignin to migrate to air interfaces and be removed at the surface of the resulting foam. It is not necessary to add surfactants. Rose and Sebald (1968) felt that foam fractionation would have application for treatment of pulp and paper wastes. However, an earlier study by NCASI #177 (1964) had tested foam fractionation as well as other foam separation techniques and concluded that foam fractionation was not feasible for decolourization of kraft bleachery effluents. There is evidence from other studies (Hayes and Munroe, 1973, Wilson and Wang, 1970, Wang et al, 1974 and Ng et al, 1971) supporting this conclusion; however, other ABSP's have been found effective.

Hayes and Munroe (1973) used dispersed air flotation of a total mill effluent which had been coagulated with alum and a cationic polymer to achieve 90% colour reduction. The method of ion flotation, which relies on the soluble anionic lignin reacting stoichiometrically with a cationic surfactant to form an insoluble precipitate, appears to be even more attractive. Application of the process to colour removal has been studied by Wilson and Wang (1970), and Wang et al (1974) in the United States and by Envirocon Ltd., (1973), Branion et al (1974), Herschmiller (1972) and Wood (1974) in Canada. In the latter study the cationic surfactant, didodecyldimethyl ammonium bromide was added to a pH adjusted (3.6 to 4.6) combined mill effluent. Batch and continuous

studies were carried out and colour removals as high as 90% were achieved. Chemical costs of the process are prohibitive and to become economically feasible, surfactant recovery is essential. To date, no attempts have been made to recover the surfactant.

2.7 Amine Extraction

The amine extraction process was originally developed and patented in France and can be applied to all common pulping effluents. The process, as applied to a bleached kraft mill, involves mixing the amine and water immiscible solvent with the effluent from the first caustic extraction stage which has been acidified to pH 3. The amines extract the coloured organic compounds and form a hydrophobic (organo-philic) precipitate which is subsequently separated by centrifugation. The amines are then regenerated for reuse by dissolving in a small volume of a caustic solution such as white liquor.

The original work carried out in France has been extended in a joint study by the Pulp and Paper Research Institute of Canada (PPRIC), Prahacs et al (1973) and Wong et al (1974). This recent research has resulted in an improved amine-solvent combination. Kemamine T-1902D, a tertiary amine, which is manufactured from fish oils and Soltrol 170, a narrow-cut hydrocarbon composed mainly of iso-tridecanes and iso-tetradecanes were found to be superior to the French system of Amberlite XAD-2/Kerosene, (i.e., achieved better colour removal at a lower cost with a lower tendency to form an emulsion). Colour removals on total mill effluents range from 50% to 80% with BOD and COD removal ranges of 10% to 35%, and 30% to 70%, respectively. Problems in the regeneration stage are the major drawback of the process. A 'third-phase' emulsion which is difficult to separate (Wong et al, 1974) is formed. Thermal treatment at 110 to 120°C appears to be the most promising method of demulsification resulting in amine recoveries of 98%. Further tests at a larger scale are planned to evaluate amine losses and other aspects.

Another version of the amine process devised by Das (1973) employs cationic primary fatty amines to precipitate the coloured organics. Initially, the amines were added in conjunction with metal salts as part of a flotation system. This proved unsuccessful, but use

of the amines alone at a dosage of 300 ppm at pH 3 to 4 formed a hydrophobic precipitate with excellent filterability. The method, when applied to a 1:1 ratio of first caustic extract:chlorination extract resulted in a reduction of 88% for colour, 67% for COD and 42% for BOD. Here again, a relatively stable emulsion forms, but a filtration method using a filter aid has shown potential for separation. Research to improve amine recycle is continuing.

Researchers in this area feel that amine extraction can be as effective as the lime treatment processes at a comparative cost. Furthermore, it does not create a sludge disposal problem. Impact on the mill is minimal. However, there would be an increased load (2% to 6%) on the evaporators and a 1% increase in lime consumption. Pilot scale research with particular emphasis on amine recycle is required before any application is made at full scale.

2.8 Membrane Processes

Included under membrane processes are reverse osmosis, dialysis, electrodialysis and ultrafiltration. The various processes can be differentiated by membrane permeability (i.e., particle size rejection) and driving force. In dialysis and electrodialysis the membranes are permeable mainly to ions. The driving force for ion diffusion is provided by a concentration difference of ions across the membrane in the former, and by an electrical potential difference in the latter. In ultrafiltration and reverse osmosis (hyperfiltration), membranes can be manufactured which are permeable to molecules of a specific size. An external pressure provides the driving force. Ultrafiltration membranes tend to be 'loose', requiring low operating pressures (10 to 15 psi) to give high flux rates for water with low rejection of inorganics, but high rejection of large molecules. On the other hand, reverse osmosis membranes are 'tight', requiring high operating pressures (600 to 1000 psi) to obtain good flux rates for water and high rejection of solutes. Reviews of membrane processes have been compiled by Cruver (1973), Lynch and Mintz (1972) and Luttinger and Hocke (1974). An excellent review of membrane processing of pulp and paper mill effluents has been prepared by Burns (1973). Dialysis was identified as not being applicable.

However, specific applications for electrodialysis, reverse osmosis and ultrafiltration have been identified with the greatest potential lying with the latter two.

One of the early proposed applications of membrane processes was for the concentration of pulp and paper mill effluents: (i) for recovery of secondary materials prior to evaporation and combustion, and (ii) for reuse of the permeate water in the mill.

The most extensive studies on reverse osmosis treatment of pulp and paper mill effluents have been described in an EPA report by Wiley et al (1972). Their conclusion that"the feasibility of employing reverse osmosis for concentrating of dilute pulping and bleaching effluents depends on developing routes to substantial improvement in the life expectancy of reverse osmosis equipment to maintain high flux rates and rejections at much lower membrane maintenance and replacement costs".... effectively summarizes the present state of the process. No cost estimates were made in this study.

Recently, EPA supported a study by Champion Papers (Fremont et al, 1973) to evaluate ultrafiltration as a method of decolourizing selected waste streams in a kraft mill. A 10,000 gpd pilot plant (Figure 22) consisting of five in-series recirculation ultrafiltration stages (spiral wound membranes) was used to decolourize the first caustic extraction stage effluent. Colour removals ranging from 90% to 97% were obtained. Colour rejection was found to be dependent upon: (i) molecular weights of colour bodies (smaller molecules were not rejected), (ii) concentration ratio (for higher concentration ratios the permeate was more coloured), and (iii) membrane type. Flux rates of 15 to 20 gal/ft²/day were achieved under optimum operating conditions. However, lower rates caused by surface fouling, membrane compaction and particulate accumulation in the membrane cartridges were common. Notwithstanding the mechanical problems encountered, the main disadvantage of ultrafiltration is the need for extensive pre-treatment (neutralization from pH 10 to 12 down to 7, cooling from 120°F to 135°F down to 100°F and filtration for suspended solids removal). Ultrafiltration does not demineralize the water as does reverse osmosis; therefore, permeate reuse is limited.

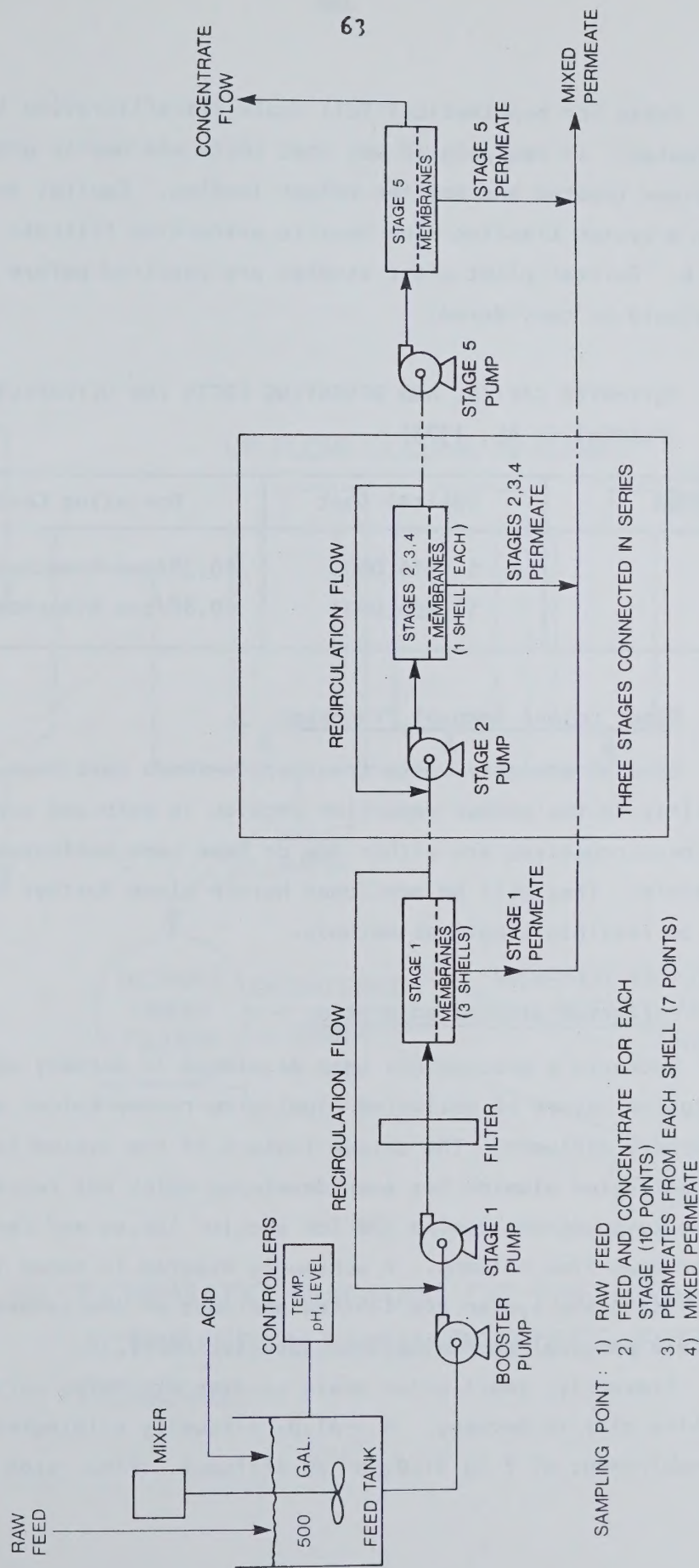


FIGURE 22. ULTRAFILTRATION PROCESS (FREMONT et al , 1973)

Costs for hypothetical full scale ultrafiltration installations were estimated. It was pointed out that costs are nearly proportional to the volume treated and not the colour loading. Capital and operating costs for a system treating pine caustic extraction filtrate are summarized in Table 6. Further pilot plant studies are required before full scale systems should be considered.

TABLE 6. ESTIMATED CAPITAL AND OPERATING COSTS FOR ULTRAFILTRATION
(FREMONT ET AL, 1973)

Flow	Capital Cost	Operating Cost
1 mgd	\$ 770,000	\$0.58/ton bleached pulp
2 mgd	\$1,250,000	\$0.88/ton bleached pulp

2.9 Other Colour Removal Processes

Several advanced waste treatment methods have been tested for applicability to the colour reduction problem in pulp and paper mills. Most of these processes are either new or have been evaluated on a limited scale. They will be mentioned herein since further development may lead to feasible treatment methods.

2.9.1 Activated alumina adsorption

Recently a process has been developed in Germany which utilizes the adsorptive nature of activated alumina to remove colour and organics from bleachery effluent. The unique feature of the system is that a granular activated alumina has been developed which has reactivity comparable to powdered alumina and low erosion losses and can be used in up flow or down flow columns. A schematic diagram is shown in Figure 23. Details on the system are limited and most of the information was obtained via personal communications (Eberle, 1974).

Presently, small pilot scale studies are being carried out at a bisulphite mill in Germany. A $\gamma\text{-Al}_2\text{O}_3$ virtually eliminates all colour with a requirement of 7 kg $\text{Al}_2\text{O}_3/\text{m}^3$ of effluent. Flow rates of 2 to 10

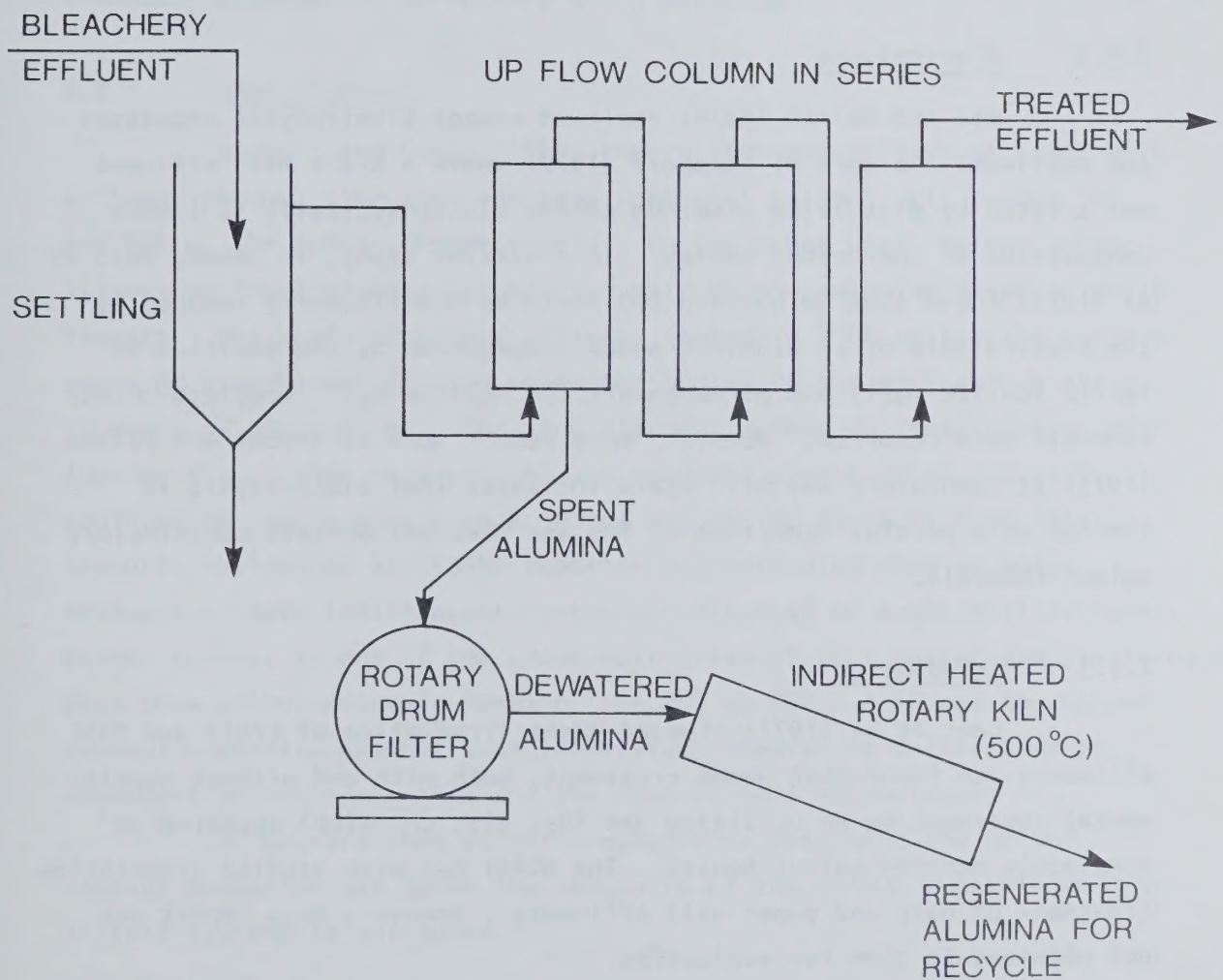


FIGURE 23. SCHEMATIC DIAGRAM OF THE GRANULAR ACTIVATED ALUMINA PROCESS FOR COLOUR REMOVAL

$\text{m}^3/\text{m}^2\text{-hr}$ in up-flow columns are reported. The optimum pH for operation of the columns is ≈ 2.5 . The spent Al_2O_3 is dewatered to 70% solids on a rotary drum filter before reactivation in a rotary kiln at 500°C .

Preliminary results indicate that the alumina can be reactivated up to 90 times without significant losses in activity. No reliable cost figures are available. However, the system has excellent potential and further evaluations are planned in Germany and in Canada.

2.9.2 Electrolysis

Wei and Heinke (1974) reviewed sewage electrolysis processes and mentioned the work of Campbell (1970) where a kraft mill effluent was treated by dissolving aluminum anodes electrolytically to induce coagulation of the colour bodies. In a similar study, in Japan, Goto et al (1971) found that colour and COD could be significantly reduced by the electrolysis of an aluminum anode accompanied by the addition of ferric ion (20 mg/l) and permanganate (40 mg/l as O_2). Complete colour removals were reported. However, more recent work by Brecht and Dalpke (1973) at laboratory and mill scale indicates that electrolysis is limited to a partial reduction of BOD and does not achieve satisfactory colour removals.

2.9.3 Irradiation

Lenz et al (1971) studied gamma irradiation of kraft and NSSC effluents and found that gamma treatment, both with and without supplemental treatment by an oxidizing gas (O_2 , air, chlorine) appeared to completely destroy colour bodies. The NCASI has also studied irradiation treatment of pulp and paper mill effluents. However, this report was not obtained in time for evaluation.

2.9.4 Adsorption on fly ash

NCASI #267 (1973) reviews some studies using fly ash for wastewater treatment. Hardwood fly ashes gave better colour removal than those from softwood because of the higher calcium oxide content of hardwood. Ninety percent colour removal from caustic extract with fly

ash dosage of approximately 25 g/l and contact times of approximately five minutes, were common. BOD and COD removals in the order of 50% were obtained. Kato and Kimura (1971) found that fly ashes containing carbon and calcium were almost as effective as activated carbon for removing lignin from kraft effluents. Another related use of fly ash has been reported by Moehle (1967) and involves its use as a sludge dewatering aid. Use of these and other waste materials for wastewater treatment purposes is definitely worth pursuing.

2.9.5 Land disposal

Blosser and Owens (1964) report that percolation of kraft mill effluent through clay loam and sand loam soil columns will remove 99% and 65% of the colour, respectively. On the other hand, colour intensification resulted when percolating calcium and ammonium-based sulphite liquors. For kraft bleachery effluent (colour = 8000 units) the authors found no significant buildup of colour bodies in the soil column after 18 weeks of application. The land disposal method is restricted by BOD loading (i.e., <400 lb/day/acre) and requires a soil pH of 6.5 to 9. In addition the soils must have a sodium adsorption ratio of 8 or less. Recently Wallace et al (1974) reported on continuing studies which evaluate a rapid infiltration system for disposal of kraft mill effluent. Colour removal is one of the prime objectives of this system and preliminary data show colour removals ranging from 20% to 98%. Although the colour removal mechanism has not been identified, removal is believed to be dependent on residence time and the type of soil encountered.

It appears that further research to determine the colour removal mechanism and hence the longevity of the colour removal capacity in soil systems is warranted.

2.10 In-Plant Colour Load Control

2.10.1 General

Recently, much of the effort in finding colour reduction methods has been aimed at eliminating the problem at the source rather than by implementing external treatment systems. Literature on internal

control measures for reducing colour load is accumulating, and has been reviewed by several authors such as Warner and Miller (1963), King (1971) and Frost (1972). In their annual reviews in the June issue of the Journal Water Pollution Control Federation, Gove and Gellman note several developments in this area and a brief summary was given recently by Gellman and Berger (1974).

Although conditions at each mill will present an unique situation requiring special attention, a number of general methods for controlling colour load at the source have been identified. These range from simple, relatively inexpensive measures requiring little change in existing technology to drastic and costly technology changes. Some of the more recent studies are discussed here.

Gellman and Berger (1974) report that preliminary findings by NCASI indicate that 33% to 50% of the total mill colour can come from the pulp mill. Measures that should reduce this contribution include:

- (i) more extensive pulp washing;
- (ii) prevention of evaporator carry-over and recycle of evaporator boilouts;
- (iii) retention of pulping liquor spills and leakage; and,
- (iv) instrumented detection of intermittent sewer losses.

The Environmental Care Project of the Swedish pulp and paper industry, designed to reduce pollution from pulp and paper mills, has stressed the importance of in-plant control measures such as minimizing accidental discharges, improving brown stock washing as well as implementing new bleaching techniques. This project is discussed by Albertson and Bergkvist (1973), Lekander (1972) and Norrstrom (1974). Similar efforts by the Finnish pulp and paper industry are reported by Malmi (1972).

Nilsson and Ahlgren (1972) suggest several measures to prevent accidental discharges. These include construction of large retention tanks, collection and recirculation of leaks and spills, installation of an alarm system to register high discharge levels and correct dimensioning of bottlenecks such as screen rooms and evaporator plants. Various process changes in kraft pulp mills to reduce pollution loads were discussed by EKONO (1972a and 1972b) and data on costs and savings of

these modifications were presented. The measures discussed include increased dilution in washing, condensate stripping, chemical spills collection, fibre spills collection and dry debarking.

Nilsson and Rennerfelt (1971) conducted a technical and economic evaluation of internal versus external pulp and paper mill waste treatment. Internal treatment was definitely preferable, but external treatment may still be necessary. The effects of various process modifications on effluent load and water usage have been evaluated by Twitchell and Edwards (1974). Several in-plant modifications requiring major technology change have been studied in detail. The more noteworthy of these are discussed below.

2.10.2 Technology change in bleaching

As mentioned previously, the bleach plant, and in particular the first caustic extraction stage, has been pinpointed as a major source of colour in pulp and paper mills. A considerable amount of research is underway to reduce this colour load by employing bleaching sequences other than the conventional CEDED or CEHDED where C = chlorination, E = caustic extraction with NaOH, D = chlorine dioxide and H = hypochlorite (either sodium or calcium). These bleaching sequence modifications and other approaches to bleach plant operations are reviewed here under their appropriate headings.

2.10.2.1 Elimination of the first caustic extraction stage.

Publications have appeared recently describing Hooker Chemical's so-called Anti-Pollution Sequence (APS I) e.g., Gall and Thompson (1973). This system involves the use of sequential addition of chlorine dioxide and chlorine (D_C) as described by Jack and Feller (1967) and Jack and Johnson (1969), followed by the substitution of sodium hypochlorite (H_{Na}) for the caustic extraction stage. The bleaching sequence is then $D_C HDED$. Gall and Thompson (1973) state that their APS I can result in colour reduction from 60% to 85% of total mill effluent using existing or slightly modified bleach plant equipment. Chemical costs are claimed to be equal or slightly higher than conventional bleach sequences while not adversely affecting pulp quality. This company is continuing work

on APS I and have also developed an APS II system which has objectives of 85% to 95% colour reduction and 75% to 85% COD and BOD reduction of bleach plant effluent. No details on APS II are available at this time, but hopefully mill trials will begin in the near future. Full scale systems of APS I are currently operating in at least four mills with three others scheduled to go on stream in the near future (Gall, 1974).

In Canada this system has been tested by Weyerhaeuser Canada Ltd., at Kamloops, B.C. The results obtained at this mill fell short of those claimed by the Hooker report and chemical costs were considerably higher.

It appears that this process change is not universally applicable, but warrants consideration among other colour control approaches.

Work on sequences similar to the Hooker ASP I is ongoing at MacMillan Bloedel Research Ltd., in Vancouver, B.C., under CPAR sponsorship. M-B Research Ltd., (1973) report on two modified bleaching sequences designated D/CHH and D/CPH involving a combined chlorine dioxide (D) and chlorine (C) stage followed by either a sodium hypochlorite (H) stage or a hydrogen peroxide (P) stage. A conventional calcium hypochlorite stage is the third stage in both.

Comparison of these sequences to the conventional CEH for semi-bleached pulp shows a 72% and an 86% colour reduction from D/CPH and D/CHH, respectively, under the best combination of operating conditions. Problems are not completely solved and work is continuing at M-B's Harmac and Port Alberni mills. Other possible sequences for semi-bleached kraft pulp being investigated by these researchers are HPH, HHP and HHH.

In addition to these, several other sequences are being studied throughout the world. For example, the Canadian Pulp and Paper Research Institute in Montreal is active in this area, currently studying several alternatives. Individual mills are experimenting with various systems. The American Can Company of Halsey, Oregon is working on a CHEH sequence (Wong, 1974). Warner and Miller reported as early as 1963 on replacing CEH by CHE at the Glatfelter mill in Spring Grove, Pennsylvania.

There is much enthusiasm in the pulp and paper industry about the potential of this approach to pollution control. It is hoped that research will continue and eventually provide a substantial decrease in the colour and other contaminant loading from the bleach plant.

2.10.2.2 Oxygen bleaching. Much of the literature on oxygen bleaching is related to the operation of a full scale plant at Enstra, South Africa (Rowlandson, 1971) and a pilot plant at Husum, Sweden (Jamieson et al, 1971). These two applications have also been discussed by Nicholls (1973).

The sequence at Husum consists of OCEDED and at Enstra, AODED, where A indicates a dilute sulphuric acid pre-treatment. Oxygen bleaching is carried out in both plants under pressure using high consistency gas-phase conditions.

Although effluent characteristics are similar to conventional bleach plant effluents, the interest in oxygen bleaching arises from the possibility of replacing chlorine-based chemicals with oxygen in the first stages of bleaching (Engstom et al, 1971 and Carpenter et al, 1973). With corrosion causing chlorides virtually eliminated, it is conceivable that the effluent from the oxygen stage (containing most of the colour and other contaminants) could be recycled to the recovery furnace. All indications are that substantial savings in both capital and operating costs of pollution control facilities should result from installation of an oxygen bleaching stage if effluent is recycled to the recovery system.

Croon (1972), Mizuguchi (1973), Rowlandson (1973) and Jamieson and Smedman (1973) all agree that oxygen bleaching can result in considerable chemical savings and reduce BOD and colour in the total mill effluent by 40% to 75% and 70% to 95%, respectively, if the liquor from the oxygen bleaching stage is recycled to the recovery furnace, thus allowing additional salt cake recovery and at the same time, destruction of coloured organics.

However, at the present time available information indicates that no recycling is being carried out at any of the four (see Table 7)

full scale installations currently in operation. The process is still in the developmental stages and its full potential is still unknown. Research is continuing by both Kamyr Corp., and Chemetics Corp., and others to further develop oxygen bleaching technology. Although capital costs are high, the potential benefits are great.

2.10.2.3 Displacement bleaching. Also known as dynamic bleaching, the displacement bleaching process involves bleaching of pulp in a continuous system in one or two towers rather than in several stages. Kamyr has developed a system using sequential chlorination (D_c) followed by EDED in one tower. A pilot unit has run in Finland at 1000 ton/day rate and at least two 500 ton/day systems have been sold in the U.S., (Collins, 1974).

Complete countercurrent washing is used, so the only water added is that entering with the chemicals. The result is a much lower effluent volume. Other advantages reported are:

- (i) reduced bleaching time needed;
- (ii) ability to pulp at a higher consistency; and,
- (iii) savings in chemical and capital cost.

Because of the complex mechanical nature of the system, maintenance problems can be anticipated as the major disadvantage.

2.10.2.4 Water conservation and reuse. Other changes in bleach plant operation based on the concept of reducing water consumption and on reusing effluents for other purposes have been proposed by several investigators.

Perhaps the most famous of these is the concept of the effluent free mill put forth by Rapson and Reeve in several papers, (e.g., Rapson and Reeve, 1972; Reeve and Rapson, 1970 and 1973). According to these researchers the elimination of bleach plant effluents in kraft mills is not only technically feasible, but more economical than effluent treatment. Fresh water requirements are reduced and discharge of wastes into receiving waters is completely eliminated.

This is done by: (i) complete countercurrent pulp washing from the bleach plant back through brown stock washing to the evaporators;

(ii) use of chlorine dioxide instead of chlorine in the first stage; (iii) removal of sodium chloride by evaporative crystallization from the white liquor; (iv) alteration in the chlorine and sodium sulphate manufacture to eliminate effluent (i.e., electrolytic production of these from recovered sodium chloride); (v) use of HCl instead of H_2SO_4 for chlorine dioxide generation; and (vi) extensive reuse of evaporator condensates.

Although not proven on a mill scale as yet, these researchers have been working closely with the Erco and Envirotech Companies to develop a full scale system. A contract for full scale demonstration of this process at the Great Lakes Paper Company in Thunderbay, Ontario, was recently awarded by the Canadian Government under the Development of Pollution Abatement Technology (DPAT) program.

Bramer (1972) discussed the benefits of closed cycle water use and stated that it is technically possible to reduce wastewater effluents to zero. This has been studied by others as well (e.g., Brecht and Dalpke, 1972 and Jacobsen, 1971) and certainly may become a reality in the future. Water reuse and recycle in bleacheries (one of the major stepping stones to achieving zero effluent) has been studied by Histed (1972) and Histed and Nicolle (1972) at the Canadian International Paper Company with CPAR support. The initial survey indicated that large reductions of water volumes and steam use are achieved by countercurrent washer flow. One mill reported that as little as 8000 gallons per ton of pulp compared to averages of 22,000 gallons were required. The latter study showed that if extensive recirculation around the chlorination stage is used in addition to countercurrent flow, a bleach plant flow of 1600 gallons per ton may be achieved. It has been observed that colour precipitation begins at these low flows. Nayak et al (1974) studied the possibility of removing colour from these concentrated bleachery effluents by lime addition. The preferred range of effluent volume was 1500 to 1700 U.S. gal/ADT for a three-step process involving: (i) acid precipitation; (ii) lime addition (2.9 g/l to 5.1 g/l); and (iii) carbonation. Ninety-five percent colour reduction on a bleachery effluent was achieved under the best conditions.

Another possibility of effluent colour improvement has been studied by Burkart (1972) whose laboratory studies indicate a potential for caustic extraction liquor reuse within the extraction stage. The concentrated effluent produced was more easily decolourized.

Mill trials by Yankowski (1972) showed that water reductions of 50% could be achieved by modified washing practice. A selective literature review of water reduction methods is also given by this author. Nelson et al (1972) also discuss current water reduction practices at several mills, including complete countercurrent washing, reuse of selective bleach plant filtrates and more judicious use of water in existing systems.

There is considerable evidence that mills are genuinely attempting to cut water use wherever possible. Such practice can only assist in colour control since removal costs are directly related to effluent volume.

2.10.3 Technology changes in pulping

Although current pulping practices (especially the kraft process) are well established in the industry and not likely to be replaced over night, there is a possibility that other pulping methods could be developed which would reduce the pollution problems associated with sulphur compounds. Pulping processes not using sulphur based chemicals have attracted considerable attention in recent years. Examples of these are holopulping and soda-oxygen pulping, which will be discussed here, as well as nitric acid pulping (Brink, 1961 and Brink et al, 1961), phenol pulping (Schweers and Rechy, 1972) and alcohol pulping (Kleinert, 1971).

2.10.3.1 Holopulping. Whitney et al (1969) have described this novel process which involves pulping with chlorine dioxide followed by extraction with alkali. Since pulping and bleaching liquors are similar in nature, they can be readily combined in a closed recovery system.

Advantages claimed include: (i) 20% to 40% higher pulp yield; (ii) rapid delignification at cooking temperatures below the

boiling point; and (iii) a minimum of air and water pollution coupled with increased chemical recovery. However, since sodium and chlorine are the main chemical residuals in the system, corrosion problems will undoubtedly have to be overcome. Electrolytic regeneration of chemicals is under investigation. Other drawbacks include high power costs and attainment of a chemical balance in the recovery. Apparently, advantages are believed to outweigh disadvantages and thus, work is continuing to develop this process for full scale application.

2.10.3.2 Soda-oxygen pulping. This process for pulping wood in mild alkali under oxygen at moderately high pressure has been under development by MacMillan and Bloedel Research Limited and others for a number of years. Originally a single-stage system was proposed, but this has been modified to an improved two-stage system. Both have been reviewed by Cox and Worster (1971). Worster et al (1971) and Worster and Pudek (1973) discuss developments and advantages of the two-stage process.

In the first stage the wood is cooked to a high yield with alkali, the pulp is then defibrized in a refiner and enters a second stage cook with alkali and oxygen. Because of the tendency for excess alkali and oxygen to attack cellulose as well as lignin, a stabilizer such as magnesium carbonate must be used in the second stage. The resulting pulp is generally comparable to kraft pulp although reduced strength seems to be the main concern. The main advantage appears to be reduced air pollution. Since no sulphur is used the production of malodorous gases as well as liquid effluents containing toxic sulphur compounds would be eliminated. The waste liquor would be evaporated and burned in the usual way in order to recover the alkali.

Another advantage of the process is that the pulp produced requires less bleaching, thus leading to less pollution from the bleach plant effluents. According to these authors, existing kraft mills could be converted to this system with the addition of equipment such as refiners for between stage defibrization, a pressure reactor for the second stage and an oxygen supply. Developmental work on this process is continuing and apparently a full scale system has been designed by M-B Research with installation at an unidentified mill underway at this time.

2.11 By-product Recovery

Current practice in kraft pulping includes incineration of kraft lignin as an integral part of the process, thus providing essential fuel value. In the case of sulphite pulping a recovery system may or may not be included. This depends on the base used in the process. Where calcium is used chemical recovery is not possible; however, by using so-called soluble bases (sodium, magnesium and ammonia) incineration is used at several mills.

Recently Sonoco (Rion et al, 1973) and Rayonier (Anon, 1972) developed systems for recovery of spent liquors from semi-chemical and sulphite pulping, respectively. These are not exactly colour reduction techniques, but colour reduction is inherent in these processes, which allow recycle of highly coloured wastes to the recovery system. Briefly, the Sonoco process uses aluminum oxide to pelletize concentrated NSSC black liquor before burning. The Rayonier process combines pulping liquors with strong caustic extract effluent before burning. A full scale application of the Rayonier process has been designed for conversion of the company's sulphite mill at Port Alice, B.C.

Aside from simply incinerating these waste liquors for heat value, there appears to be a tremendous potential for utilizing portions of this replenishable resource (mainly lignins). The availability, preparation and uses for organic by-products formed in pulping processes have been thoroughly discussed by Hoyt and Goheen (1971) and several others.

Currently, several companies are recovering useful by-products from pulping liquors and at the same time reducing the pollutant load to receiving waters. For example, the Ontario Paper Company at Thorold, Ontario, uses fluidized bed treatment, ion exchange and evaporation to produce ethyl alcohol and salt cake. It is also one of four sulphite mills in North America producing vanillin. Kraft lignin is recovered by the Westvaco mill at Charleston, South Carolina and another company, Crown Zellerback Corporation at Bogalusa, Louisiana processes black liquor for the production of dimethyl sulphoxide. Crude turpentine recovery is practiced at several mills including the Harmac mill of MacMillan Bloedel and several mills such as the Hodge,

Louisiana mill of Continental Can Co., recover tall oil from kraft wastes.

The list of uses for lignin and other pulping by-products is almost endless. Hoyt and Goheen (1971) discuss the utilization of lignin products including use for oil well drilling muds, cement and concrete additives, dispersants, grinding aids, binders and adhesives, and many others. Patents, such as a process for making building material from lime treated spent sulphite liquor (Silby, 1972) are appearing continuously.

With research into concentrating techniques such as reverse osmosis and electrodialysis proceeding at a rapid rate, the feasibility of using pulping wastes for more profitable means than burning for their fuel value seems closer. The main problem appears to be in finding efficient, economical ways of separating the waste liquors into usable fractions. Several patents such as one by Brauns (1967) for recovering lignosulphonates have dealt with this, but much more research is needed. This requires better understanding of lignin chemistry as well as further studies on the nature of pulping effluents and concentration techniques.

3 INVENTORY OF PILOT SCALE AND FULL SCALE COLOUR REMOVAL INSTALLATIONS

As part of this review, an inventory of ongoing or completed colour removal pilot and full scale investigations was compiled. This inventory is presented in Table 7, and by no means is it an exhaustive summary. It must be realized that a great deal of research is being carried on by individual mills, and unfortunately, this information is generally restricted to internal use. Therefore, many pilot scale and even some full scale studies are never reported in the literature. Information on developments in other countries is often difficult to obtain. The list in Table 7 is felt to include most full scale systems and some of the more significant pilot scale studies.

TABLE 7. INVENTORY OF FULL SCALE AND PILOT SCALE COLOUR REMOVAL INSTALLATIONS

PROCESS	LOCATION	COMMENTS
Minimum Lime	Georgia Pacific - Woodland, Maine	Full Scale (Down at time of report)
Minimum Lime	Georgia Pacific - Crossett, Arkansas	Full Scale - Intermittent Use
Minimum Lime	Interstate Paper - Riceboro, Georgia	Full Scale - Continuous
Minimum Lime	Continental Can - Hodge, Louisiana	Full Scale - Continuous
Massive Lime	International Paper - Springhill, Louisiana	Large Scale - Not in Operation
Modified Lime (Lime Mud)	" " "	" " " " "
Lime	Calcasieu Paper - Elizabeth, Louisiana	Full Scale - Testing
Alum	Gulf State Paper - Tuscaloosa, Alabama	Full Scale - Developmental Stage
Alum	Lake Baikal, U.S.S.R.	Full Scale - Continuous
Alum	Several Mills in Sweden	Full Scale - Continuous
Iron-Lime	Mill in Japan	Full Scale - Continuous
Lime Seawater	Nova Scotia Research	Pilot Scale - Testing
Uddeholm-Kamyr	Daishowa Paper Co. - Iwanuma, Japan	Full Scale - Continuous
Uddeholm-Kamyr	Uddeholm - Skoghall, Sweden	Full Scale - Continuous
Uddeholm-Kamyr	Several Mills in North America	Mobile Pilot Plant
Rohm and Haas	Several Mills in North America	Mobile Pilot Plant
Activated Carbon	St. Regis Paper - Pensacola, Florida	Large Scale Testing
Reverse Osmosis	Green Bay, Wisconsin	Large Scale Testing
Ultrafiltration	Champion Papers - North Carolina	Large Scale Testing
Kamyr Oxygen Bleaching	Enstra, South Africa	Full Scale
Kamyr Oxygen Bleaching	Cellulose d'Aquitaine - Aquitaine, France	Full Scale
Chemetics Oxygen Bleaching	Chesapeake Corporation - West Point, Virginia	Full Scale
Chemetics Oxygen Bleaching	Aspa, Sweden	Full Scale
Modified Bleaching	MacMillan-Bloedel - Nanaimo, B.C.	Large Scale Testing
Modified Bleaching	Glatfelter - Spring Grove, Pa.	In-Plant Changes
Hooker APS I	Several Mills in North America	Full Scale at Four Mills
Kamyr Displacement Bleaching	Two Full Scale Systems sold in U.S. - Texas and North Carolina	Piloted in Sweden and Finland
Extensive Chemical Recovery	Ontario Paper - Thorold, Ontario	Production of Vanillin - One of Four Mills in North America

4 DISCUSSION OF THE COLOUR PROBLEM

4.1 Significance of Colour Characteristics to the Design of Colour Removal Facilities

Since no two mill effluents are alike, it is unlikely that any one method of treatment will be suitable for all. Furthermore, it can be expected that the specific colour characteristics will have some effect on the efficiency of virtually all colour removal techniques. Specifically, it has been shown that:

- (i) Lime precipitation does not remove low molecular weight molecules.
- (ii) During activated carbon adsorption the low m.w. materials are more readily adsorbed than higher m.w. substances.
- (iii) Different carbons preferentially adsorb different molecule sizes according to the pore structure of the carbon (i.e., pore radii in the range 20 to 150 Å remove the larger m.w. constituents and pores ≤ 10 Å radii are primarily responsible for removal of low m.w. species). These two studies point out the importance of knowing the molecular size of particles to be removed before selecting a suitable adsorption medium.
- (iv) Membrane processes remove large m.w. colour molecules more easily than low m.w. colour molecules.
- (v) Although biological treatment is largely ineffective for removing colour there is evidence that low m.w. colour molecules decrease and a shift toward larger m.w. species occurs, especially during extended aeration (Obiaga and Ganczarczyk, 1972). Since lime treatment is particularly effective in removing high m.w. colour molecules, it would seem logical that any system combining biological and chemical treatment should be sequenced to take advantage of changes in m.w. distribution, i.e., biological treatment followed by lime treatment. In fact, where lime and biological systems do exist, the reverse order is used (i.e., at Riceboro and Hodge).

Optimization of this combination has never been studied, but should be looked at in the near future.

- (vi) The nature of the colour bodies (i.e., solubility in alkaline solutions) is such that they are not well adsorbed from alkaline systems. Therefore, adsorption on resin or carbon is optimum at acidic pH values. Fuchs (1964) and others observed better percent colour removals as pH is decreased.
- (vii) The negative charge on these colour molecules makes them susceptible to chemical coagulation with positively charged metal ions. Although much of the work on colour removal has been aimed at chemical treatment, little effort has been spent in determining the relation between particle mobility (zeta potential) and coagulant dosage in order to optimize colour removal.

These are some of the fundamental factors that must be considered when designing a colour removal system.

Since different methods have higher efficiency for certain m.w. species, it is reasonable to consider a combined treatment system composed of individually assembled unit processes to achieve a final low level of colour (i.e., biological-chemical-adsorption). Lime treatment followed by activated carbon adsorption has been shown to be compatible (Sanks, 1973, and Kabeya et al, 1973), but further developmental work is required. Optimum systems cannot be developed on the basis of present knowledge of the nature of colour and mechanisms of colour removal.

4.2 Internal Mill Changes and Effluent Treatment

Throughout the world there is a trend toward more stringent pollution control legislation. This is affecting the pulp and paper industry by forcing advanced wastewater treatment of mill effluents to remove residual dissolved organics including coloured materials. Some regions have a seasonal water shortage or other water supply problems. Thus, it is advantageous, even necessary, to recycle and reuse process

water wherever possible to conserve water. Even where water supply is not a problem, there is an industry-wide trend toward decreased water use and increased recycling and reuse. This is achieved by cutting water consumption to a minimum and renovating used process water for reuse in other parts of the mill. Decolourization must be included in any renovation scheme and can be attained by either internal process changes or external treatment in a number of ways.

It is advantageous to reduce the effluent volume to a minimum since it has been proven that colour can be removed more efficiently from concentrated waste streams. Also, colour removal costs are more proportional to volume treated than to loading or concentration.

Reduction of colour loading at the source by in-plant modifications has real potential. The modifications can range from simple relatively inexpensive measures such as better pulp washing and better 'housekeeping' practices to complex technology changes such as implementation of oxygen bleaching.

There are many opportunities in a pulp and paper mill to exercise in-plant control of colour and effluent recycling, but each mill is a special case. Aside from identifying the general changes that can be made, each mill must be examined individually. This is done in most mills and terms such as 'tightening up' water use or 'closing the system' are now commonplace.

Of course, the ultimate goal from a pollution control point of view is the concept of 'zero discharge'. Predictions have been made that this will be required by 1985 in some countries, including the United States and South Africa. Several researchers believe it to be technically feasible now, but large scale trials have not been carried out as yet. Much work remains to be done on this aspect, but it is apparent that the average discharge from pulp and paper mills has decreased considerably over the past 20 years.

Of all the in-plant modifications, changes in the bleach plant seem to have the most immediate potential for colour reduction. Elimination of the caustic extraction stage can be done in a number of ways with only minor changes in a conventional bleachery. Oxygen bleaching requires more radical and expensive changes, but since the

waste can be sent to the chemical recovery system, the disposal problem is solved. At the same time valuable chemicals are saved. Other innovations such as displacement bleaching may prove to be acceptable methods of achieving concentrated effluents facilitating external treatment processes.

Recovery of spills in the pulp plant is another area of importance when considering in-plant colour reduction.

Several novel pulping processes are being developed that could lower pollution. Among these, only soda-oxygen pulping and holopulping are likely to be applied in the near future. Even these processes will likely achieve only limited use for quite some time because kraft pulping is firmly established as a chemical pulping process.

While in-plant changes should be considered and implemented, as a first preference, external treatment may often still be required. There are a large number of external treatment methods which are known to be technically feasible for colour removal from pulp and paper mill effluents. Chemical treatment methods based on precipitation with Ca^{++} , Mg^{++} , Al^{+++} , Fe^{+++} or some combination of these, alone or with flocculating agents have advanced to the stage of full scale application. The same is true of the resin separation method of Uddeholm-Kamyr. The Rohm and Haas resin process, membrane processes (both ultrafiltration and reverse osmosis) and activated carbon adsorption have been tested on a large scale, while certain foam separation techniques, ozonation, and extraction with amines have been examined at laboratory scale. These processes are known to be technically feasible, but the question of economics remains to be answered by further pilot and full scale testing. Several other methods for colour removal have been and are being investigated. These include irradiation treatment, adsorption on fly ash and other waste materials, adsorption on activated alumina, electrolysis, land disposal and biological treatment. From preliminary studies, further work on most of these methods is warranted and is indeed in progress.

It is safe to say that colour removal technology, although advancing rapidly, is still in its infancy. There is room for innovation

in this aspect of wastewater treatment. Many methods are known to work, but due to the wide range of effluents in the industry, no one method is likely to be applicable to all types. Therefore, research is continuing to develop many viable treatment alternatives.

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